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Kinetics and thermal properties of epoxy resins containing the ionic liquid \([\text{C}_6\text{mim}]\text{FeCl}_4\)

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The 1-hexyl-3-methylimidazole ferrum tetrachloride salt \([\text{C}_6\text{mim}]\text{FeCl}_4\) and mixed amines were blended in different mass ratios with bisphenol-A epoxy resin E-51 to obtain a series of cured products at room temperature. The thermal decomposition of the cured products was studied by thermogravimetric analysis, dynamic mechanical analysis, and in situ Fourier-transform infrared spectroscopy. The thermal degradation temperatures changed as a function of different mass ratios of \([\text{C}_6\text{mim}]\text{FeCl}_4\). The kinetics of thermal decomposition were then analyzed by the Flynn-Walle-Ozawa method.

The results show that the incorporation of \([\text{C}_6\text{mim}]\text{FeCl}_4\) is a better way to improve the performance of room-temperature curing epoxy resins.

1. Introduction

Epoxy resin is one of the most important industrial reactive materials because of their excellent properties and low cost. They have been widely explicated in the fields of coatings, adhesives, composites, laminates and encapsulates[1-3]. As a classic engineered polymer[4-5], epoxy resin has drawn attention due to the wide applications including in photocuring[6], magneto resistive materials[7], magnetic materials[8], and epoxy nanocomposites. They also have versatile physicochemical properties in otherwise inert polymers and can enhance the mechanical properties and reduce flammability[9].

In recent decades, epoxy systems containing ionic liquid (ILs)[10-11] have attracted increased academic interest because of their thermostability under high temperature. Currently, most work has focused on the modification of epoxy resins in ionic liquid to investigate the characteristics of ILs and promote cross-linking of epoxy resins[12-13]. Kowalczyk et al. used 1-butyl-3-methylimidazolium tetrafluoroborate \((\text{Bmim})\text{BF}_4\) as a latent hardener to study the mechanical properties of cured products[14]. Rahmathullah et al. used \([\text{Emim}]\text{N(CN)}_2\) as a thermally latent hardener of epoxy resins to measure the effect of \([\text{Emim}]\text{N(CN)}_2\) on the curing behavior and properties of the resulting polymer network[15]. Maka et al. studied both the influence of the size of the imidazolium cation and the type of anion on the reactivity of epoxy resin/ionic liquid systems as well as the thermomechanical properties[16]. Guo et al. used 1-butyl-3-methylimidazolium hexafluorophosphate \((\text{Bmim})\text{PF}_6\) as a dispersant in the epoxy resin/expanded graphite composites and observed subtle changes in the activation energy \((E_a)\) of epoxy resin/graphite composites/[Bmim]PF₆[17]. However, there are relatively few studies into the basic theories of the thermal properties and degradation kinetics in which ILs act as curing agent to initiate epoxy resin cross-linking. This is especially true for 1-hexyl-3-methylimidazole ferrum tetrachloride salt \([\text{C}_6\text{mim}]\text{FeCl}_4\).

In our previous work[18], \([\text{C}_6\text{mim}]\text{FeCl}_4\) compound with mixed amines as a new hardener was used to initiate epoxy resin E-51 cross-linking reaction at room temperature (25°C). This curing system shows remarkably better thermostability and thermomechanical properties than that of the aliphatic amine as a hardener[19]. Further studies of the kinetics and thermal properties of this room temperature curing system including the thermogravimetric and dynamic mechanical analysis are performed.

2. Kinetic methods

The non-isothermal experiments were performed with a thermobalance, and the sample mass was measured as a function of temperature. The rate of degradation or conversion, \(da/dt\), is a linear function in a temperature-dependent rate constant, \(k\), and a temperature independent function of conversion, \(\alpha\):

\[
da/dt = k f(\alpha)
\]

(1)

The reaction rate constant, \(k\), is described by the Arrhenius expression

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

(2)

where \(A\) is the pre-exponential factor, \(E\) is the activation energy, \(R\) is the gas constant, and \(T\) is the absolute temperature. The combination of Eqs. (1) and (2) gives
\[
\frac{da}{dt} = \alpha \exp(-\frac{E}{RT}) \quad (3)
\]

If the temperature of the sample is changed by a controlled and constant heating rate, \( \beta = \frac{dT}{dt} \), then the variation in the degree of conversion can be analyzed as a function of temperature. This temperature is dependent on the time of heating. Therefore, the rearrangement of Eq. (3) gives

\[
\frac{da}{d\alpha} = \frac{\alpha f(\alpha) \exp(-\frac{E}{RT})}{\beta} \quad (4)
\]

The integrated form of Eq. (4) is generally expressed as

\[
g(\alpha) = \frac{\alpha f(\alpha) \exp(-\frac{E}{RT})}{\beta} \quad (5)
\]

where \( g(\alpha) \) is the integrated form of the conversion dependence function. We applied integral kinetic methods according to the aforementioned equations.

The integral method involves an approximate integration of Eq. (5) for the Flynn-Wall-Ozawa method\(^{[19,20]} \) using Doyle approximation\(^{[21]} \) for the integration. This has been expressed as:

\[
\log g = \log \left( \frac{\alpha f(\alpha)}{\beta} \right) - 2.315 - 0.456 \frac{E}{RT} \quad (6)
\]

Using Eq. (6) the linear representation of \( \log g \) versus \( 1/T \) allows us to determine the activation energy with a given value of the conversion.

### 3. Experimental

#### 3.1 Materials

The \([\text{C}_2\text{mim}]\text{FeCl}_4\) is synthesized in our laboratory according to the literature\(^{[23]} \). Technical grade diglycidyl ether of bisphenol-A (E-51, epoxide equivalent weight=196 g/epoxide) was supplied by Nantong Chemicals Industry Co. Ltd., China. Mixed amines (diamino diphenyl methane (DDM): m-phenylenediamine (m-PDA)=2:3) were purchased from Chinese Medicine Reagent Co. Ltd., (Beijing), China. The aliphatic amine hardener: zc-20, zc-30, and zc-50 cashew oil-modified amine curing agent and tetraethylene pentamine (TEPA) were purchased from Xuzhou Technology Co. Ltd., China.

#### 3.2 Curing procedure of epoxy resins

\([\text{C}_2\text{mim}]\text{FeCl}_4\) and mixed amines are used as curing agents. At first, E-51 is blended with mixed amines at 5:1, then 2 wt.%, 10 wt.%, and 15 wt.\% \([\text{C}_2\text{mim}]\text{FeCl}_4\) is added to the epoxy resin system. The compositions of the aliphatic amine epoxy systems are listed in Table 1. All mixtures were poured separately into hot aluminum molds and then cured at room temperature (25°C) for 4 h and then post-cured at 150°C for 2 h. The reaction process of E-51 and \([\text{C}_2\text{mim}]\text{FeCl}_4\) is:

\[
\text{FeCl}_4^- + \text{H}_3\text{C}-\text{N}-\text{N} \rightarrow \begin{array}{c}
\text{R}_1 \\
\end{array} + \text{FeCl}_4^- + \text{H}_3\text{C}-\text{N}-\text{N} \rightarrow \begin{array}{c}
\text{R}_1 \\
\end{array}
\]

#### 3.3 Measurements

The thermogravimetric analysis (TGA) is carried out by an apparatus of the USA TA company Number 970501.901 under the nitrogen atmosphere with a purge rate of 50 ml/min. Heating rates of 5, 10, 15 and 20°C/min are used. For each experiment approximately 6–8 mg sample is used in the TGA test. In situ FTIR spectra are recorded with a MAGNA-IR 750 spectrometer (Nicolet Instrument Co. U.S.A.). The KBr method is used for measuring the in situ FTIR spectra ranging from 300°C to 450°C at the heating rate of 5°C/min. Dynamic mechanical analysis (DMA) is carried out on a Rheometric Scientific instrument in air at a heating rate of 5°C/min. The specimen of 8×40 mm is loaded in a single cantilever mode with a frequency of 1 Hz.

### 4. Results and discussion

#### 4.1 Reaction characteristic of epoxy resins containing \([\text{C}_2\text{mim}]\text{FeCl}_4\)

Fig. 1 shows the results of DSC measurement with a heat rate of 5°C/min. The exothermic peak temperature \( (T_p) \) refers to the curing temperature, and the \( T_p \) of EM-0, EMC-2, EMC-5, EMC-10, EMC-15 are 142, 65, 56, 60 and 65°C, respectively. The \( T_p \) value of epoxy resins is down from 142°C to 65°C by incorporation of \([\text{C}_2\text{mim}]\text{FeCl}_4\), and the minimum value is corresponding to the epoxy resin containing 5 wt.% amount of \([\text{C}_2\text{mim}]\text{FeCl}_4\). It is worth noting that the EMC-2 sample has one more exothermic peak at 130°C, according to the article\(^{[18]} \), the epoxy curing reaction containing \([\text{C}_2\text{mim}]\text{FeCl}_4\)
involves two stages. First, the tertiary amine N atom on the imidazole ring attacks the C atom on the epoxy group to facilitate 1:1 nucleophilic addition. Next, the negative oxygen ion facilitated epoxy ring opening, and the quaternary amine structure on the ring combine to trigger an epoxy cross-linking reaction. So the exothermic peak at 130 °C derives from the second stage of curing reaction. This indicates that [C₆mim]FeCl₄ reacting with mixed-amine to form new curing agent, they exhibit apparently synergistic effect on the curing process of these epoxy resins.

4.2 Thermal properties and decomposition kinetics of cured epoxy resins

<table>
<thead>
<tr>
<th>Samples</th>
<th>T₅% (°C)</th>
<th>T₅₀ (°C)</th>
<th>T_max (°C)</th>
<th>Char yield at 500°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMC-2</td>
<td>310</td>
<td>354</td>
<td>344</td>
<td>23</td>
</tr>
<tr>
<td>EMC-5</td>
<td>306</td>
<td>344</td>
<td>333</td>
<td>25</td>
</tr>
<tr>
<td>EMC-10</td>
<td>284</td>
<td>335</td>
<td>315</td>
<td>28</td>
</tr>
<tr>
<td>EMC-15</td>
<td>280</td>
<td>329</td>
<td>312</td>
<td>30</td>
</tr>
</tbody>
</table>

In our previous work,[19] room temperature epoxy materials were cured by aliphatic amines and started to thermally degrade at 250~280°C. However, epoxy systems containing [C₆mim]FeCl₄ with different mass ratios (EMC-2 and EMC-5) begin to degrade at ~310°C. The initial thermal decomposition temperature was compared to the aliphatic amine curing systems and increases at least 30°C. This illustrates that the epoxy systems contain a higher percentage of [C₆mim]FeCl₄ and exhibit relatively lower thermostability. The maximum thermal degradation temperature is about 340°C. However, epoxy resins containing a higher percentage of [C₆mim]FeCl₄ lead to relatively higher char yields at 500°C.

To get the kinetic information, such as the activation energy, this TGA study was conducted with different heating rates. Figs. 3-6 show the TGA thermograms of the epoxy resins containing different mass ratios of [C₆mim]FeCl₄. These correspond to the dynamic experiments carried out at different heating rates (5, 10, 15, and 20 °C/min). For all samples, the TGA curves shift to higher temperatures with increasing heating rate despite having similar shapes.
The activation energy of EMC-2, EMC-5, EMC-10, and EMC-15 at 5% conversion is about 33 kJ/mol. According to the calculation results, EMC-5 has the highest activation energy at the same conversion. E-51 is likely completely cured because it contains 5wt% [C₆mim]FeCl₄. On the other hand, the steric hindrance of the reaction is due to unreacted [C₆mim]FeCl₄. This makes complete curing difficult and may lead to a lower thermal decomposition activation energy. Although synergistic effects of [C₆mim]FeCl₄ and mixed amines have been observed from the high activation energy of EMC-5 at degradation ratios of 0.2-0.5, the incorporation of [C₆mim]FeCl₄ components would decrease the activation energy in early stages and increase in the later stages. This means that [C₆mim]FeCl₄ components influence the degradation behaviors of the epoxy resin.

4.3 FTIR studies
To further investigate the degradation process and details, in situ FTIR was used to monitor the thermal degradation of EMC-5 from 300°C to 450°C. Fig. 7 shows the FTIR spectra of residual products of EMC-5 at different temperatures. All the absorption peaks of the FTIR spectra can be found at 300°C, which is consistent with the TGA results. The absorption band of the aliphatic chain at 1295 cm⁻¹ decreased quickly with increasing temperature. It then disappears at 320°C. There is no new visible absorption band during the thermal degradation period. On the other hand, the absorption peak at 1179 cm⁻¹ starts to decrease slowly. The absorption peaks at 1106 cm⁻¹, 1034 cm⁻¹, and 1236 cm⁻¹ for ester groups as well as the band at 1179 cm⁻¹ disappeared at the 340°C. This indicates that the degradation of EMC-5 below 340°C mainly results from the destruction of C-O-R groups in the polymer matrix. At 370°C, the band of aromatic nuclei at 1608 cm⁻¹, 1510 cm⁻¹, 1456 cm⁻¹, and 828 cm⁻¹ decrease quickly and then disappear at 390°C. When the temperature is 450°C, there are a few new infrared peaks including 1590 cm⁻¹ (C=N) and the absorption band of imidazole ring at 1438 cm⁻¹. These peaks imply the existence of ionic liquid [C₆mim]FeCl₄ in the polymer network configuration. All of these data suggest that the degradation pattern of epoxy resin has been changed due to the incorporation of [C₆mim]FeCl₄ component. Although the degradation activation energy of EMC-5 is lower at initial stages, most of them remain as nitrogenous compounds in the materials at higher temperature. These compounds promote the formation of cross-linking char to protect the inner structure. Thus, they can slow down the rate of weight loss and increase activation energy at high temperature.

The unit of activation energy $E_a$ is kJ/mol, the correlation coefficient is represented by $R^2$:

<table>
<thead>
<tr>
<th>Conversion $\alpha$</th>
<th>EMC-2</th>
<th>EMC-5</th>
<th>EMC-10</th>
<th>EMC-15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>$R^2$</td>
<td>$E_a$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.05</td>
<td>33</td>
<td>0.98</td>
<td>35</td>
<td>0.97</td>
</tr>
<tr>
<td>0.1</td>
<td>41</td>
<td>0.99</td>
<td>42</td>
<td>0.98</td>
</tr>
<tr>
<td>0.2</td>
<td>42</td>
<td>0.99</td>
<td>44</td>
<td>0.99</td>
</tr>
<tr>
<td>0.3</td>
<td>43</td>
<td>0.98</td>
<td>45</td>
<td>0.99</td>
</tr>
<tr>
<td>0.5</td>
<td>44</td>
<td>0.98</td>
<td>55</td>
<td>0.99</td>
</tr>
</tbody>
</table>
The DSC analyses indicate that epoxy resins containing [C₆mim]FeCl₄ require lower curing temperatures. Increasing decomposition temperatures compared with aliphatic amine curing systems at least 30 °C according to the TGA results. The thermal degradation kinetics of epoxy resins containing [C₆mim]FeCl₄ were studied by TGA. The temperature of decomposition and weight loss rates are tuned by [C₆mim]FeCl₄. The FTIR measurements evaluated the evolution of the chemical structures during decomposition. The results indicate that the incorporation of [C₆mim]FeCl₄ reduces the activation energy at an initial stage of the degradation and increased it at later stages of the degradation. This confirms that [C₆mim]FeCl₄ components influence the degradation behaviors of epoxy resin. Therefore, the addition of the [C₆mim]FeCl₄ into one component of the epoxy resins is a better way to improve the performance of room-temperature curing epoxy resins.

Notes and references

Kinetics and thermal properties of epoxy resins containing the ionic liquid \([\text{C}_6\text{mim}]\text{FeCl}_4\)

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