RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Kinetics and thermal properties of epoxy resins containing the ionic liquid [C6mim]FeCl4

Changmei Zheng,[a] Meihua Liu,[a] Yuan Yin,[a] Yifan Zhang,[a] Wei Wei,[a]* Pengyang Deng,[a] Chunbai Zheng,[a]*

Polymer Composites Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

The 1-hexyl-3-methylimidazole ferrum tetrachloride salt ([C6mim]FeCl4) and mixed amines were blent 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 [C6mim]FeCl4. The kinetics of thermal decomposition were then analyzed by the Flynne-Walle-Ozawa method. The results show that the incorporation of [C6mim]FeCl4 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], magnetoresistive 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 ([Bmim]BF4) as a latent hardener to study the mechanical properties of cured products[14]. Rahmathullah et al. used [Emim]N(CN)2 as a thermally latent hardener of epoxy resins to measure the effect of [Emim]N(CN)2 on the curing behavior and properties of the resulting polymer network[15]. Maka et al. studied both the influences 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 ([Bmim]PF6) as a dispersant in the epoxy resin/expanded graphite composites and observed subtle changes in the activation energy (E_α) 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 ([C6mim]FeCl4).

In our previous work[18], [C6mim]FeCl4 compound with mixed amines as a new hardener was used to initiate epoxy resin E-51 cross-linking reaction at room temperature (25℃). 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, $d\alpha/dt$, is a linear function in a temperature-dependent rate constant, k, and a temperature independent function of conversion, α:

$$d\alpha/dt = k f(\alpha) \qquad (1)$$

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

$$K = A\exp(-E/RT) \qquad (2)$$

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

[a.] *Polymer Composites Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.*

Email: weiwei@ciac.ac.cn, zhengcb@ciac.ac.cn; Fax:86-431-85262839; Tel: 86-431-85262329;

dα/dt=A exp(-E/RT) f(α)   (3)

If the temperature of the sample is changed by a controlled and constant heating rate, β= 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

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) exp(-\frac{E}{RT})$$ (4)

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

$$g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T exp\left(-\frac{E}{RT}\right) dT$$ (5)

where g(α) 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:

$$log\beta=log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - 0.4567\frac{E}{RT}$$ (6)

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

## 3. Experimental

3.1 Materials

The [C_6mim]FeCl_4 is synthesized in our laboratory according to the literature [23]. Technical grade diglycidyl ether of bisphenol-A (E-51, epoxide equivalent weights=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

[C_6mim]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.%, 5wt.%, 10wt.%, and 15 wt.% [C_6mim]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℃)for 4 h and then post-cured at 150℃ for 2 h. The reaction process of E-51 and [C_6mim]FeCl_4 is:
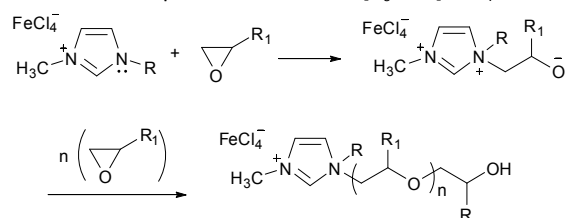
3.3 Measurements

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℃/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℃ to 450℃ at the heating rate of 5℃/min. Dynamic mechanical analysis (DMA) is carried out on a Rheometric Scientific instrument in air at a heating rate of 5℃/min. The specimen of 8 × 40mm is loaded in a single cantilever mode with a frequency of 1Hz.

Tab 1 Compositions of epoxy systems

Epoxy samples	Curing composition (wt %)				
	E-51	zc-20	zc-30	zc-50	TEPA
EZ-20	100	50	0	0	0
EZ-30	100	0	53	0	0
EZ-50	100	0	0	100	0
ET	100	0	0	0	13
Epoxy samples	Curing composition (wt %)		
	E-51	Mixed amines	[C_6mim]FeCl_4
EM-0	100	20	0
EMC-2	100	20	2.4
EMC-5	100	20	6
EMC-10	100	20	12
EMC-15	100	20	18

4. Results and discussion

4.1 Reaction characteristic of epoxy resins containing [C_6mim]FeCl_4
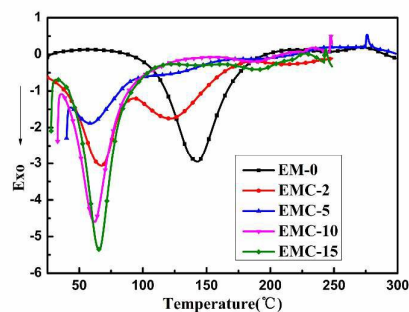

Fig. 1 DSC curves of curing process of epoxy resins

Fig.1 shows the results of DSC measurement with a heat rate of 5℃/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℃, respectively. The Tp value of epoxy resins is down from 142℃ to 65℃ by incorporation of [C_6mim]FeCl_4, and the minimum value is corresponding to the epoxy resin containing 5wt% amount of [C_6mim]FeCl_4. It is worth noting that the EMC-2 sample has one more exothermic peak at 130℃, according to the article[18], the epoxy curing reaction containing [C_6mim]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℃ derive from the second stage of curing reaction. This indicates that [C_6mim]FeCl$_4$ 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

Tab 2 Typical temperatures of loss of mass for epoxy samples

Samples	$T_{5\%}$ (℃)	$T_{50\%}$(℃)	T_{max}(℃)	Char yield at 500℃(%)
EMC-2	310	354	344	23
EMC-5	306	344	333	25
EMC-10	284	335	315	28
EMC-15	280	329	312	30

In our previous work[19], room temperature epoxy materials were cured by aliphatic amines and started to thermally degrade at 250～280℃. However, epoxy systems containing [C_6mim]FeCl$_4$ with different mass ratios (EMC-2 and EMC-5) begin to degrade at ~310℃. The initial thermal decomposition temperature was compared to the aliphatic amine curing systems and increases at least 30℃. This illustrates that the epoxy systems contain a higher percentage of [C_6mim]FeCl$_4$ and exhibit relatively lower thermostability. The maximum thermal degradation temperature is about 340℃. However, epoxy resins containing a higher percentage of [C_6mim]FeCl$_4$ lead to relatively higher char yields at 500℃.
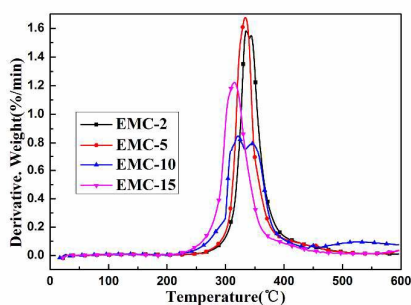

Fig.2 DTG curves of all samples at the heating rate of 10℃/min

Apparently, the TGA curves of the composites have only one peak at three temperatures (Fig. 2). The degradation process can be divided into four stages. The first phase occurs from 40℃ to 280℃ and consists of thermal decomposition of the epoxy resin. The thermal decomposition is characterized by segmentation of random chains and terminal chains that lead

to the loss of hydrogen atoms and other organic groups at a low molar mass. The second phase (from 280℃ to 330℃) is attributed to the acceleration of the thermal decomposition of the epoxy resin during which carbon chains begin to form. These byproducts of the epoxy resin are decomposed into gas and porous carbon chains. The third phase (between approximately 330℃ and 400℃) consists of a thermal decomposition of the remaining epoxy resin. The fourth phase started at 400℃ and was due to oxidization of the carbon chain that formed during the combustion process of the epoxy resin.

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 [C_6mim]FeCl$_4$. These correspond to the dynamic experiments carried out at different heating rates (5, 10, 15, and 20℃/min). For all samples, the TGA curves shift to higher temperatures with increasing heating rate despite having similar shapes.
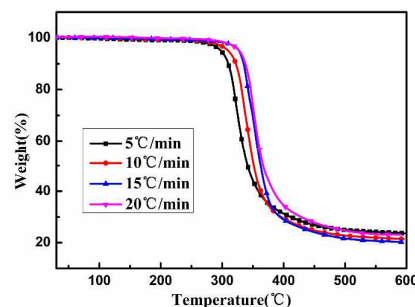
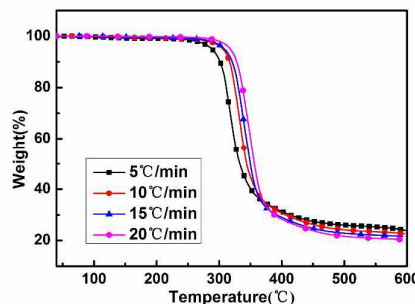

Fig.3 TGA curves of EMC-2 at different heating rates

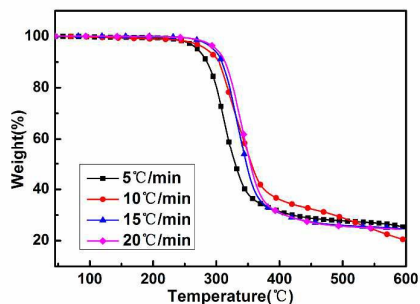**Fig.4** TGA curves of EMC-5 at different heating rates

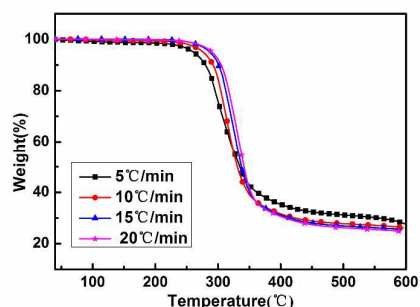**Fig.5** TGA curves of EMC-10 at different heating rates

Fig.6 TGA curves of EMC-15 at different heating rates

We used the Flynne-Walle-Ozawa[20-22] method to calculate the activation energy. In this method, different points correspond to different conversion values. This method is widely used to determine the decomposition activation energies at defined conversion values. At a given value of the conversion, the activation energy can be obtained from a logarithmic plot of heating rates as a function of the reciprocal of temperature. The slope of such a line is given by $-0.4567E/RT$. Here, conversion values of 5, 10, 20, 30, and 50 are used. All calculated activation energies are listed in Table 3.

Tab 3 Calculated activation energies at various conversions of the decomposition

| Conversion α	EMC-2		EMC-5		EMC-10		EMC-15	
	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2
0.05	33	0.98	35	0.97	28	0.99	33	0.99
0.1	41	0.99	42	0.98	34	0.98	34	0.99
0.2	42	0.99	44	0.99	42	0.98	41	0.97
0.3	43	0.98	45	0.99	43	0.97	42	0.99
0.5	44	0.98	55	0.99	43	0.95	43	0.96

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

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℃ to 450℃. 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℃, 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℃. There is no new visible absorption band during the thermal degradation period. On the other hand, the absorption peak at

$$H_3C-\underset{\underset{|}{\overset{H}{C}}}{}-CH_3$$
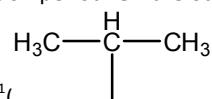
1179cm⁻¹ ( ) starts to decrease slowly. The absorption peaks at 1106 cm⁻¹, 1034 cm⁻¹, and 1236 cm⁻¹ for ester groups as well as the band at 1179 cm⁻¹ disappear at the 340℃. This indicates that the degradation of EMC-5 below 340℃ mainly results from the destruction of C-O-R groups in the polymer matrix. At 370℃, the band of aromatic nuclei at 1608 cm⁻¹, 1510cm⁻¹, 1456cm⁻¹, and 828cm⁻¹ decrease quickly and then disappear at 390℃. When the temperature is 450℃, 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.
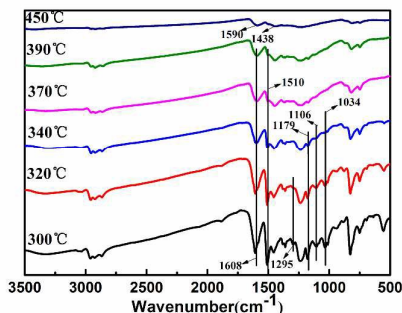
Fig .7 FTIR spectra of EMC-5 during the thermal degradation from 300 to 450℃

4.4 DMA analysis of cured epoxy resins

The dynamic mechanical analysis (DMA) measurements of these epoxy resins are shown in Fig. 8. The glass transition temperatures (T_g) of ET, EZ-20, EZ-30, and EZ-50 are 132, 80, 91, and 56℃ as determined by the peak temperature of the tan δ curve. The Tg of EMC-2, EMC-5, EMC-10, and EMC-15 are 157, 150, 137, and 126 ℃. These are all higher than the ET. These results may be caused by the introduction of an imidazole ring structure into cross-linking network of the epoxy resins. Moreover, the Tg values of these epoxy resins decreased with increasing $[C_6mim]FeCl_4$ content. This may be caused by the increase in the content of the unreacted $[C_6mim]FeCl_4$ in the cross-linking network of the epoxy resin.
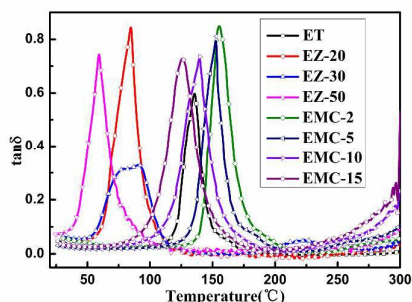

Fig.8 DMA curves of the cured epoxy resins

5. **Conclusions**

The DSC analyses indicate that epoxy resins containing $[C_6mim]FeCl_4$ require lower curing temperatures. Increasing decomposition temperatures compared with aliphatic amine curing systems at least 30℃ according to the TGA results. The thermal degradation kinetics of epoxy resins containing $[C_6mim]FeCl_4$ were studied by TGA. The temperature of decomposition and weight loss rates are tuned by $[C_6mim]FeCl_4$. The FTIR measurements evaluated the evolution of the chemical structures during decomposition. The results indicate that the incorporation of $[C_6mim]FeCl_4$ reduces the activation energy at an initial stage of the degradation and increased it at later stages of the degradation. This confirms

that $[C_6mim]FeCl_4$ components influence the degradation behaviors of epoxy resin. Therefore, the addition of the $[C_6mim]FeCl_4$ into one component of the epoxy resins is a better way to improve the performance of room-temperature curing epoxy resins.

Notes and references

1   M.L. Sun, L.Y. Wu. *Machine Press*, 2002, **4**.
2   P. Chen, S.P. Liu, D.J. Wang. *Chemical Industry Press*, 2011, **1**.
3   B. Jiang, Y.D. Huang. *Composites Part A: Applied Science and manufacturing*, 2008, **39**, 712-717.
4   B. Jiang, Y.D. Huang. *Analytica Chimea Acta*, 2008, 103-108.
5   H.B. Gu, J. Guo, H.G. Wei et al. *Journal of Materials Chemtstry C*, 2015, **3**, 8152.
6   M. Sangermano, M.A. Tasdelen, Y. Yagci. *Polymer Chemistry*, 2007, **45**, 4914-4920.
7   H.B. Gu, J. Guo, H.G. Wei et al. *Advanced Materials*, 2015, **27**, 6277-6282.
8   J.N. Huang, Y.H. Cao, X. Zhang et al. *Aip Advances*, 2015, **5**, 0971831-15.
9   X. Zhang, X.R. Yan, J. Guo et al. *Journal of Materials Chemistry C*, 2015, **3**, 162.
10 P. Marija, R. Kenneth, N. Luis Paulo et al. *Chemical Society Reviews*, 2011, **40**, 1383.
11 J.D. Holbrey, K.R. Seddon. *Clean Products and Processes*, 1999, 223.
12 B. Wang, Y.R. Kang, L.M. Yang et al. *Journal of Molecular Catalysis A: Chemical* 2003, **203** , 29.
13 O. Bortolini, V. Conte, C. Chiappe et al. *Green Chemistry*, 2002, **4** , 94.
14 K. Kowalczyk, T. Spychaj. *Industrial Chemistry Research*, 2003, **48** , 833.
15 M. Rahmathullah, A. Jeyarajasingam, Merritt et al. *Macromolecules*, 2009, **9**, 3219.
16 H. Maka, T. Spychaj, R. Pilawka. *Industrial Engineering Chemistry Research*, 2012, **51**, 5197.
17 B. Guo, J. Wan, Y. Lei et al. *Journal of physics D: applied physics*, 2009, **42**, 1.
18 M. Yuqin, W. Wei, Z. Changmei, et al. *Applied Chemistry*, 2015, 32, 636.
19 H. Sanming, W. Wei, Y. Tianbo, et al. *Applied Chemistry*, **20150223**.
20 J.H. Flynn, L.A. Wall. *J Res Nat Bur Stand A Phys Chem*, 1996, **70**, 487.
21 T. Ozawa. *Bull Chem Soc Jpn* 1965, **38**, 1881.
22 C.D. Doyle. *Nature*, 1965, **207**, 240.
23 L. Xiaohua, Y. Fuming, Z. Qing et al. *Process Engineering Journal*, 2010, **4** , 789.

Graphic:

Kinetics and thermal properties of epoxy resins containing the ionic liquid [C$_6$mim]FeCl$_4$

Changmei Zheng, Meihua Liu, Yuan Yin, Yifan Zhang, Wei Wei*, Pengyang Deng, Chunbai Zheng *
Polymer Composites Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
E-mail: zhengcb@ciac.ac.cn
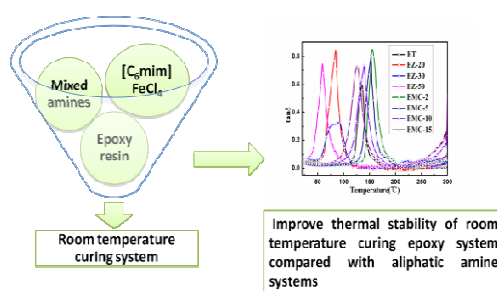
The 1-hexyl-3-methylimidazole ferrum tetrachloride salt ([C$_6$mim]FeCl$_4$) and mixed amines were blended in different mass ratios with bisphenol-A epoxy resin E-51 to obtain a series of cured products at room temperature. The TGA and DMA results of this system show that the incorporation of [C$_6$mim]FeCl$_4$ is a better way to improve the performance of room-temperature curing epoxy resins.