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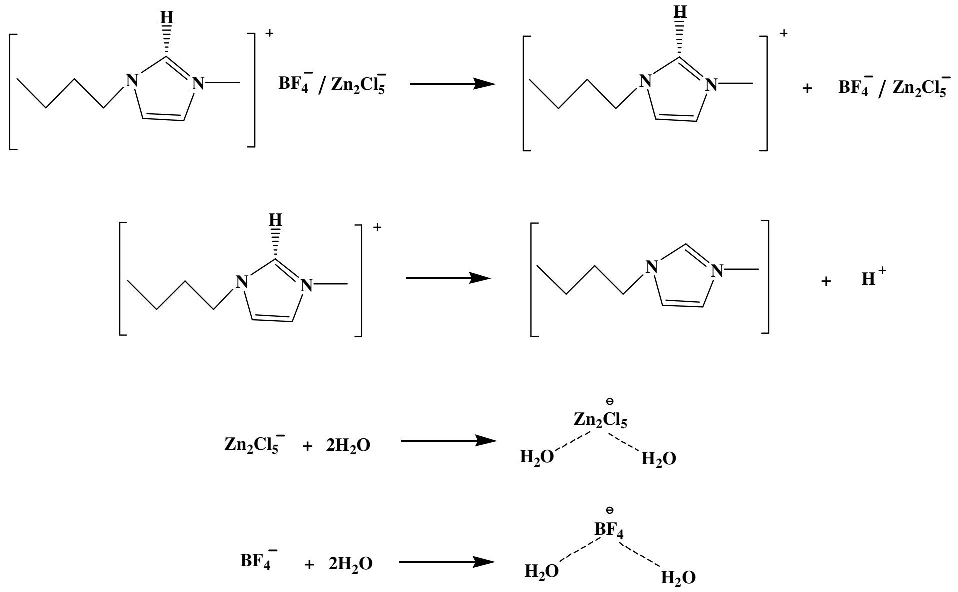

The [Bmim]BF_4 and [Bmim]Cl/$x$$ZnCl_2$($x$=0.67) ionic liquids could improve the decomposition ratio, which was attributed to the ionized H^+ from $[Bmim]^+$, participated in the breakage process of ester and ether bonds. Meanwhile, the decomposition kinetics of resin system in near-critical water was also studied.

The Effect of Ionic Liquids on Decomposition Behavior of Epoxy Resin in Subcritical Water

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Abstract: The effect of ionic liquids on decomposition behavior of E-51/MeTHPA system in subcritical water condition was studied. The effects of ionic liquid types and dosage on decomposition ratio were investigated in detail. The results showed that [Bmim]BF_4 and [Bmim]Cl/$x$$ZnCl_2$($x$=0.67) could improve the decomposition ratio of resin system, and [Bmim]Cl/$x$$ZnCl_2$ (x=0.67) was more efficient. Meanwhile, the promotion mechanism of ionic liquid for decomposition ratio was analyzed. The decomposition kinetics study of E-51/MeTHPA system showed that the reaction order of resin system without ionic liquids was 0.8301 in subcritical water condition, while with the addition of 20wt%[Bmim]BF_4 and [Bmim]Cl/$x$$ZnCl_2$($x$=0.67), the reaction order n was 0.6727 and 0.6602, respectively.

Key words: Epoxy resin; Ionic liquids; Subcritical water; Promotion mechanism;

Decomposition kinetics;

1. Introduction

Epoxy resin, as a typically thermosetting plastic, has been widely applied in adhesive, automobile, aerospace, electronic circuit board laminates, etc [1,2], due to its extraordinary properties. Therefore, decomposition and recovery of waste epoxy resin can have prominent economic benefit and environmental significance. However, epoxy resin with three-dimensional network structure is practically insoluble in most conventional solvents, so it is difficult to recycle the waste resin by using conventional method [3]. In recent years, super critical water and subcritical water have been considered environmental and effective methods to decompose epoxy resin, due to the fact that water is nontoxic, cost-effective, readily available [4, 5].

It is well known that the dissociation constant of water increases 3 orders of magnitude from room temperature to subcritical state, so the subcritical water has a strong ability of ionization and the concentration of hydrogen ions (H^+) or hydroxyl ions (OH^-) is higher than that at room temperature, which can play a certain degree of acid-base catalysis in hydrolysis reaction of polyester or ether substances. Therefore, some waste polymers can be degraded using subcritical water method [6-8].

In our previous studies [9], the decomposition of epoxy model compounds, containing ether bond and bisphenol-A structure in the subcritical water condition was studied and the decomposition mechanism was proposed based on decomposition products for the model compounds. *A. Ikeda et al* [10] researched the decomposition of polycarbonate in subcritical water at 200–300℃. The main products were phenol, bisphenol A, and p-isopropenylphenol. The reaction was accelerated by the addition of Na_2CO_3, and the yield of identified products reached 68% in the reaction at 250℃.

Ionic liquid (ILs), as a non-aqueous, aprotic or protic and polar solvent, is consist of an organic cation with an inorganic or organic anion and have a wide liquids temperature range [11]. Ionic liquids, as a new class of green solvents for practical applications in decomposition and recovery of waste polymers, have attracted growing academic and industrial interest because of their unique properties: negligible vapor pressure, high conductivity, excellent thermal stability, chemical stability, good ability to dissolve organic and inorganic compounds, wide electrochemical window, which are considered as very promising replacements for the traditional organic solvents [12-15]. *K.I. Park et al* [16] investigated the catalytic decomposition of poly lactic acid (PLA) with alkyl phosphonium-based ionic liquid and the results showed that ionic liquid had good plasticizing and catalytic decomposition for PLA. *P. Zhu et al* [17] separated and recovered materials from waste printed circuit boards by degrading bromine epoxy resins using ionic liquid and the results showed that hydrogen bond of ionic liquid [Emim][BF_4] played an important role in dissolving bromine epoxy resins.

In the present study, subcritical water and ionic liquid was used together to decompose the cured E-51/MeTHPA system. The effect of ionic liquids on decomposition behavior of E-51/MeTHPA system in subcritical water condition was investigated in detail and the promotion mechanism of ionic liquid for decomposition reaction was analyzed. Meanwhile, the decomposition kinetics of E-51/MeTHPA system in subcritical water condition was studied as well.

2. Experimental

2.1 Materials

Commercial diglycidyl ether of bisphenol A type epoxy resin (E-51) was supplied by Wuxi Resin Factory, China. Methyl tetrahydro phthalic anhydride (MeTHPA) and benzyl dimethylamine (BDMA) were commercially available. 1-butyl-3-methyl imidazole chloride ([Bmim]Cl) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) were purchased from Shanghai D.B Chemicals Co., Ltd. Zinc chloride ($ZnCl_2$) was provided from Tianjin Yong Da Chemicals Co., Ltd. All of the other analytical chemicals were purchased from Chemical Reagent Company of Harbin.

The preparation of [Bmim]Cl/$x$$ZnCl_2$ (mole fraction, x=0.67) was shown in Scheme.1. Detailed procedure are as follows: weighed a certain amount of [Bmim]Cl and $ZnCl_2$, respectively and put them into a sealed container. The solid mixture was heated by using microwave oven (Power, 200W) until it melted completely and formed sticky homogeneous system and then cooled down to room temperature. Finally, the obtained product was [Bmim]Cl/$x$$ZnCl_2$.

Scheme.1

Scheme.1 The prepared route of ionic liquid [Bmim]Cl/$x$$ZnCl_2$

2.2 Preparation of E-51/MeTHPA sample

The epoxy resin (E-51), the curing agent (MeTHPA) and accelerant (BDMA) were mixed according to a mass ratio of 100:84.7:1 and then injected into the stainless steel mold before reaching the gel time. The mixture was cured at 100℃ for 2h and then heated to 150℃ for another 5h. Finally, the cured epoxy resin was cut into cubic samples with size of 20mm×20mm×2mm.

2.3 Decomposition experiment of E-51/MeTHPA sample

The decomposition experiment could be reference to our previously reported literature [18]. The volume of the removable stainless steel reactor was 100 mL and the feedstock ratio of resin sample, ionic liquid and distilled water was 1g: 0.2g: 10mL. The reaction was carried out at 270℃ for 45 min in a subcritical condition. The liquid decomposition products were collected and analyzed by GC-MS. The solid residues were immersed in acetone for 24 h, washed 3 times with distilled water and dried at

100℃ for 24 h in a vacuum oven. The decomposition ratio of resin sample could be calculated by equation (1). The decomposition ratio was averaged with each experiment repeated three times.

$$a = \frac{M_i - M_t}{M_i} \times 100\% \quad (1)$$

Where a is the decomposition ratio, M_i is original mass of resin, and M_t is the mass of the dried solid residue after degradation.

2.4 Characterization

The cured degree of E-51/MeTHPA was measured by differential scanning calorimeter (DSC, TA Q200, USA). The sample was heated from 25℃to 200℃ at the heating rate of 10℃/min under nitrogen atmosphere.

Thermo-gravimetric test (TGA, ZRP-2Y) was carried out at 270℃ for 90 min with the air atmosphere to discuss the thermal oxidation decomposition of the E-51/MeTHPA system.

The acidic type of ionic liquids was determined by using Fourier transform infrared spectroscopy (FT-IR, VERTEX 70) using pyridine as a probe (Py-IR). The wavelength ranged from 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

The composition and distribution of liquid decomposition products of E-51/MeTHPA system were measured by GC-MS (6890/5973N, USA) equipped with HP-5MS Elastic quartz capillary column (30m×0.25m×0.25μm) was used. The operating conditions were as follows: injection temperature and ion source temperature were 280℃ and 230℃, respectively. The high purity helium was used as carrier gas at the flow rate of 1.0 ml/min and the column temperature was from 50℃ to 280℃ with heating rate of 10℃/min. The scanning range of MS was 0-500amu and electron ionization source was 70eV.

3. Result and discussion

3.1 The DSC analysis of E-51/MeTHPA system

The cured degree of E-51/MeTHPA could be measured by DSC. Fig.1 represents the DSC curve of E-51/TETA system. As shown in Fig. 1(a), it was observed that the glass transition temperature (T_g) of cured resin system was 132℃ and the post curing peak could not be observed in the DCS curve, indicating that the E-51/MeTHPA system was cured completely

Fig. 1

Fig. 1 The DSC curves of cured epoxy resin system before and after decomposition

3.2 The thermo-gravimetric analysis of E-51/MeTHPA system

The thermo-gravimetric test was carried out in the air atmosphere to discuss the influence of the thermal oxidation decomposition on the E-51/MeTHPA system. Fig. 2 shows the thermo-gravimetric curve of the E-51/MeTHPA system at 270℃ for 90 min. From the Fig. 2, it was clearly found that the weight loss of the E-51/MeTHPA system was less than 3％ in the process of heat treatment for 90 min, indicating that the thermal oxidation had little impact on decomposition of resin system.

Fig. 2

Fig. 2 The thermo-gravimetric curve of the E-51/MeTHPA system at 270℃ for 90min

3.3 The determination of acidic type of ionic liquids

The acidic type of ionic liquids was determined by FT-IR using pyridine as a probe (Py-IR)[19]. Pyridine could react with Brønsted and Lewis acids to form the cation $[PyH]^+$ and Py-Lewis complex, respectively. By observing the two absorption peak of $[PyH]^+$ and Py-Lewis complex near 1540 cm^{-1} and 1450 cm^{-1} in the FT-IR spectra respectively, the acidic type of ionic liquids could be determined. From the

Fig. 3, it could be clearly found that the two characteristic absorption peaks near 1540 cm^{-1} or 1450 cm^{-1} did not appear in the FT-IR spectrum of $[Bmim]BF_4$+Py, indicating that $[Bmim]BF_4$ itself had no acidity. Nevertheless, in the FT-IR spectrum of $[Bmim]Cl/xZnCl_2$+Py (x=0.67), the obvious characteristic absorption peak near 1450cm^{-1} appeared, suggesting $[Bmim]Cl/xZnCl_2$ (x=0.67) ionic liquid showed Lewis acidity.

Fig. 3

Fig. 3 The Py-IR spectra of ionic liquids

3.4 The effect of ionic liquids on decomposition ratio of E-51/MeTHPA system

3.4.1 Effect of ionic liquid types

In order to investigate the effect of various ionic liquids on the decomposition ratio of the E-51/MeTHPA system, two types of ionic liquids were added into reaction system, respectively. The additive amount of ionic liquid was 20wt％ (0.2g) of resin mass (1g). Table.1 illustrates the effect of various ionic liquids on the decomposition ratio of the E-51/MeTHPA system in subcritical water. As indicated in Table.1, Both $[Bmim]BF_4$ and $[Bmim]Cl/xZnCl_2$(x=0.67) ionic liquids could improve the decomposition ratio of resin system. Compared with no ionic liquid, the decomposition ratio increased 3.81％ and 10.76％, respectively.

Table. 1 The effect of various ionic liquids on decomposition ratio of E-51/MeTHPA system in subcritical water (270℃, 45min).

Types of ionic liquids	Dosage (wt％)	Decomposition ratio (%)	Pressure (MPa)
No ionic liquid	---	17.29	5.4
$[Bmim]BF_4$	20	21.10	5.3
$[Bmim]Cl/xZnCl_2$ (x=0.67)	20	28.05	5.3

wt％ is the mass ratio of ionic liquid to epoxy resin (1g resin, 0.2g ionic liquid and 10ml water).

3.4.2 Effect of ionic liquid dosage

The results in Fig. 4 and Fig. 5 show the effect of [Bmim]BF_4 and [Bmim]Cl/xZnCl_2 (x=0.67) dosage on decomposition ratio of resin system. As shown in Fig.4, it was clear that the decomposition ratio of resin system had no significant improvement with the increase of [Bmim]BF_4 dosage. When [Bmim]BF_4 dosage increased to 284wt％， the decomposition ratio improved only 10％. Therefore, changing the dosage of [Bmim]BF_4 had little impact on the decomposition ratio of resin system. Nevertheless, as could be seen from Fig.5, it was observed that the decomposition ratio almost reached the maximum value (28.05％) with 20wt％ [Bmim]Cl/xZnCl_2 dosage, while [Bmim]Cl/xZnCl_2 dosage was less or more than 20wt％, which would be adverse to improving the decomposition ratio of resin system.

Fig. 4

Fig. 4 The effect of [Bmim]BF_4 dosage on decomposition ratio of E-51/MeTHPA system

Fig. 5

Fig. 5 The effect of [Bmim]Cl/xZnCl_2 dosage on decomposition ratio of E-51/MeTHPA system

3.5 The analysis of decomposition products of E-51/MeTHPA system

3.5.1 The DSC analysis of residual resin

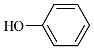
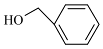
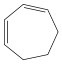
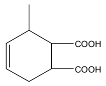
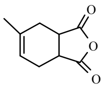
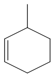
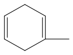
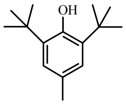
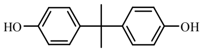
The residual of E-51/MeTHPA system after decomposition was studied by DSC. As shown in Fig. 1(b), the glass transition temperature (T_g) of residual resin was almost 60℃. Compared with original epoxy resin, the T_g reduced by 72℃, indicating that the crosslink degree of residual resin decreased, resulted from the fracture of crosslink bond in the process of decomposition.

3.5.2 The analysis of liquid decomposition products

The liquid decomposition products in acetone phase were analyzed by GC/MS. Table.2 presents the main components and relative content of the liquid decomposition products with 20wt％various ionic liquids in subcritical water condition. As indicated in Table 2, without ionic liquid, the main decomposition products included phenol, bisphenol A and other phenolic substances, generated from the breakage of ester bond in the main chain, as well as anhydrides and aromatic dicarboxylic acid, formed from the breakage of cross-linked bonds between the resin and curing agent.

With the addition of 20wt％[Bmim]BF_4 ionic liquid, bits of cycloolefin were generated in addition to the above mentioned products and the contents of phenolic substances and anhydride related substances were basically the same, indicating that [Bmim]BF_4 was more advantageous to promote the breakage of ether bond in the main chain. At the same time, the content of 2, 6-di-tert-butyl-*p*-cresol increased, which indicated that [Bmim]BF_4 was advantageous to the rearrangement of residual groups of C-C bond breakage. While 20wt％[Bmim]Cl/$x$$ZnCl_2$ ionic liquid was added into reaction system, the species of decomposition products increased. The total content of phenolic substances decreased, while that of anhydride related substances increased, which accounted for 16％ and 75％, respectively, indicating that [Bmim]Cl/$x$$ZnCl_2$ was advantageous to the breakage of crosslink ester bond. Meanwhile, the cycloolefin, generated from decarboxylation reaction and methyl rearrangement of anhydride related substances, accounted for 28％, indicating that the decomposition process was accompanied by a variety of side reactions.

Table.2 The main components and relative content of liquid decomposition products with various ionic liquids (270℃, 45min, 20wt%ILs)

Products	Structure	No ILs	[Bmim]BF_4	[Bmim]Cl/xZnCl_2
Phenol		9.70%	17.8%	13.45%
Benzyl alcohol		4.50%	----	0.36%
1,3-cycloheptadiene		----	----	4.21%
3-methyl-4-cyclohexene-1,2-dicarboxylic acid		13.24%	13.58%	1.99%
Methyl-tetrahydro-phthalic anhydride		15.34%	19.15%	44.98%
3-methyl-cyclohexene		----	5.21%	21.70%
1-methyl-1,4-cyclohexadiene		----	----	2.00%
2,6-di-tert-butyl-*p*-cresol		8.77%	10.09%	1.21%
Bisphenol A		15.4%	3.70%	0.70%

3.6 Promotion mechanism of ionic liquids for decomposition ratio

According to the GC-MS analysis and our previous studies[18], the general decomposition process of E-51/MeTHPA system in subcritical water condition could be described in the Scheme.2. In subcritical water condition, H_2O generated the protonation effect and hydronium ion (H_3O^+) was formed, due to the increase of H_2O ionization degree. The ether bond in the main chain and the crosslink ester bond were broken under the action of hydrolysis, which combined with the active hydrogen or hydroxide ions to generate stabilized small molecular substances, such as bisphenol A and aromatic dicarboxylic acid, as indicated the path 1, 2 in Scheme.2. The bisphenol A was broken under the action of pyrolysis, which combined with residual groups of C-C bond breakage in the main chain to produce phenol, alkyl substituted phenol or alcohol, as indicated the path 3 in Scheme.2.

Scheme.2

Scheme.2 The decomposition process of E-51/MeTHPA system in subcritical water [18]

Accordingly, $[Bmim]BF_4$ and $[Bmim]Cl/xZnCl_2$ would ionized the imidazole cation ($Bmim^+$) and the corresponding anion (BF_4^-, $Zn_2Cl_5^-$) in subcritical water, as indicated in Scheme.3. $[Bmim]^+$ could dissociate parts of H^+ so that the system could exhibit weak acidity[20], while the ionized anion formed hydrogen bonds with H_2O molecule[21, 22]. Therefore, with the addition of $[Bmim]BF_4$ and $[Bmim]Cl/xZnCl_2$ ionic liquids, H^+ from $[Bmim]^+$ dissociation participated in the breakage process of path 1, 2 in Scheme.2 and played a promotion effect on epoxy decomposition.

Scheme.3

Scheme.3 The ionization of $[Bmim]BF_4$ and $[Bmim]Cl/xZnCl_2$ and interaction with H_2O

However, the improvement of decomposition ratio of resin system with $[Bmim]Cl/xZnCl_2$ was higher than that with $[Bmim]BF_4$, because the nucleophilicity of $Zn_2Cl_5^-$ anion was stronger than that of BF_4^- anion[23], which could further attack the electron-deficient carbon of carbonyl in the cross-linked ester bonds to catalyze ester bond breakage and the aromatic carboxylic acid was produced, as indicated (1) in Scheme.4. Besides, the presence of $Zn_2Cl_5^-$ was also accompanied with many complex side reactions. For example, $Zn_2Cl_5^-$ could attack the carbon of carboxyl in anhydride curing agent to form the carbanion. After undergoing the decarboxylation and rearrangement reactions, cycloolefin substances were produced, as indicated (2) in Scheme.4.

Scheme.4

Scheme.4 The catalytic decomposition reaction of $Zn_2Cl_5^-$ in subcritical water

3.7. The decomposition kinetics of E-51/MeTHPA system

In subcritical water condition, assuming the reaction order of decomposition reaction of epoxy resin (*EP*) was *n*, the reaction rate equation could be given as

$$-\frac{d[EP]}{dt} = k \cdot f([EP] \cdot [H_2O]) \qquad (2)$$

Where *k* is decomposition reaction rate constant, and *t* is decomposition reaction time. In the decomposition process, H_2O was used as reaction medium, whose concentration could be considered to be constant. Furthermore, the *EP* was solid, so the concentration of *EP* could be substituted with the mass of *EP*. Therefore, the equation (2) could be expressed as

$$-\frac{dEP_m}{dt} = k_1 \cdot f(EP_m) \qquad (3)$$

Where k_1 is equal to $k \cdot [H_2O]$, and EP_m is residual mass after decomposition. After the introduction of decomposition ratio (a), the equation (3) becomes

$$\frac{da}{dt} = k_1 \cdot f(1-a) \qquad (4)$$

Where $f(1-a)$ is equal to $(1-a)^n$ and the equation (4) is carried on indefinite integral, so the equation (4) could be expressed as

$$a = k_2 \cdot t^{\frac{1}{1-n}} + C \qquad (5)$$

Nonlinear curve fit was obtained by plotting a vs. t^m, and the reaction order (n) was calculated by equation (6).

$$n = 1 - \frac{1}{m} \tag{6}$$

Without ionic liquids, the effect of reaction time on decomposition ratio of resin system was indicated in Fig.6. It was clearly that the decomposition ratio increased with the increase of reaction time and just reached 95.86% within 55min. After the fit of the experiment data, it could be observed that the curve fit well and the fit equation was obtained. According to the equation (6), the reaction order n was calculated and the value was 0.8301.

Fig. 6

Fig. 6 The effect of reaction time on decomposition ratio without ILs (270℃)

Furthermore, Fig.7 shows the influence of reaction time on decomposition ratio of resin system with addition of 20 wt%[Bmim]BF_4 It was also found that the decomposition ratio completely reached 100% within the same time of 55 min, indicating that ionic liquid had a promotion effect on decomposition ratio of resin system. After the fit of the experiment data, the reaction order n was also determined and the calculated value was 0.6727. Similarly, when 20wt%[Bmim]Cl/$x$$ZnCl_2$ was added into reaction system, the decomposition ratio completely reached 100% within 53 min, as indicated in Fig. 8. After the fit of the experiment data, the calculated reaction order n was 0.6602.

Fig. 7

Fig. 7 The effect of reaction time on decomposition ratio with 20wt%[Bmim]BF_4 (270℃)

Fig. 8

Fig. 8 The effect of reaction time on decomposition ratio with 20wt％[Bmim]Cl/*x*$ZnCl_2$ (270℃)

4. Conclusions

This work investigated the effect of ionic liquids on decomposition behavior of E-51/MeTHPA system. Some conclusions could be drawn as follows:

(1) [Bmim]BF_4 and [Bmim]Cl/*x*$ZnCl_2$(x=0.67) could improve the decomposition ratio of resin system, and [Bmim]Cl/*x*$ZnCl_2$(x=0.67) was more efficient. Changing the dosage of [Bmim]BF_4 had little impact on the decomposition ratio of resin system, while the decomposition ratio almost reached the maximum value (28.05％) with 20wt％[Bmim]Cl/*x*$ZnCl_2$ dosage.

(2) GC-MS results showed the main components and relative content of decomposition products varied with the ionic liquid types, indicating that ionic liquid types played an important role in breakage position of resin system.

(3) With the addition of [Bmim]BF_4 and [Bmim]Cl/*x*$ZnCl_2$ ionic liquids, the improvement of decomposition ratio was attributed to the ionized H^+ from $[Bmim]^+$, participated in the breakage process of ester and ether bonds. However, the improvement of the decomposition ratio with [Bmim]Cl/*x*$ZnCl_2$ was higher than that with [Bmim]BF_4 , because the nucleophilicity of $Zn_2Cl_5^-$anion was stronger than that of BF_4^-anion, which could further catalyze ester bond breakage.

(4) The reaction order of resin system without ionic liquids was 0.8301 in subcritical water, while with the addition of [Bmim]BF_4 and [Bmim]Cl/*x*$ZnCl_2$ (x=0.67), the reaction order was 0.6727 and 0.6602, respectively

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Caption

Fig. 1 The DSC curves of cured epoxy resin system before and after decomposition

Fig. 2 The thermo-gravimetric curve of E-51/MeTHPA system at 270℃ for 90min

Fig. 3 The Py-IR spectra of ionic liquids

Fig. 4 The effect of [Bmim]BF_4 dosage on decomposition ratio of E-51/MeTHPA system

Fig. 5 The effect of [Bmim]Cl/*x*$ZnCl_2$ dosage on decomposition ratio of E-51/MeTHPA system

Fig. 6 The effect of reaction time on decomposition ratio without ILs (270℃)

Fig. 7 The effect of reaction time on decomposition ratio with 20wt％[Bmim]BF_4 (270℃)

Fig. 8 The effect of reaction time on decomposition ratio with 20wt％[Bmim]Cl/*x*$ZnCl_2$ (270℃)

Table.1 The effect of various ionic liquids on decomposition ratio of E-51/MeTHPA system in subcritical water (270℃, 45min)

Table.2 The main components and relative content of liquid decomposition products with various ionic liquids (270℃, 45min, 20wt％ILs)

Scheme.1 The prepared route of ionic liquid [Bmim]Cl/*x*$ZnCl_2$

Scheme.2 The decomposition process of E-51/MeTHPA system in subcritical water

Scheme.3 The ionization of [Bmim]BF_4 and [Bmim]Cl/*x*$ZnCl_2$ and interaction with H_2O

Scheme.4 The catalytic decomposition reaction of $Zn_2Cl_5^-$ in subcritical water

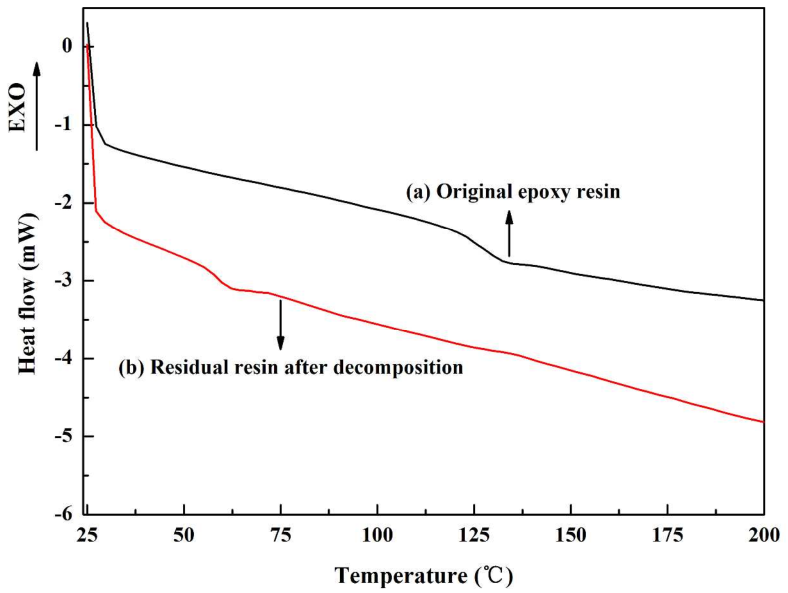


Fig. 1 The DSC curves of cured epoxy resin system before and after decomposition
296x209mm (300 x 300 DPI)

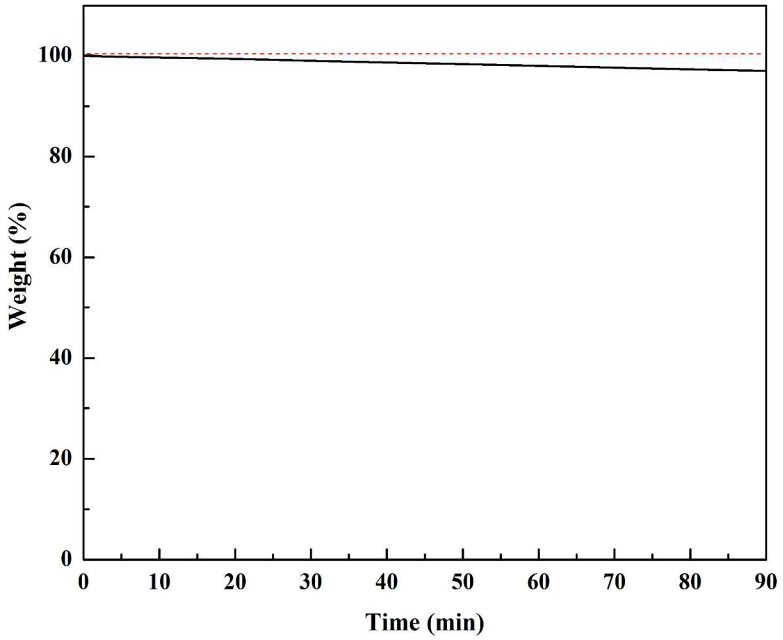


Fig. 2 The thermo-gravimetric curve of E-51/MeTHPA system at 270℃ for 90min
279x215mm (300 x 300 DPI)

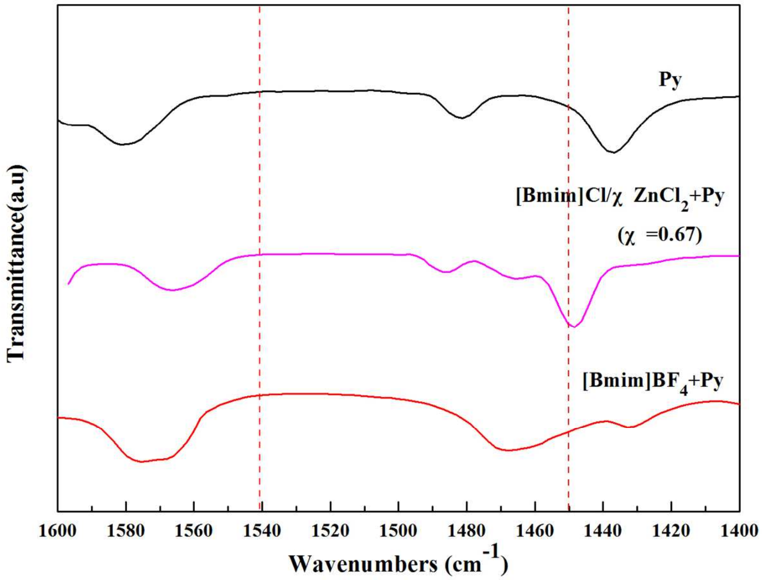


Fig. 3 The Py-IR spectra of ionic liquids
297x209mm (150 x 150 DPI)

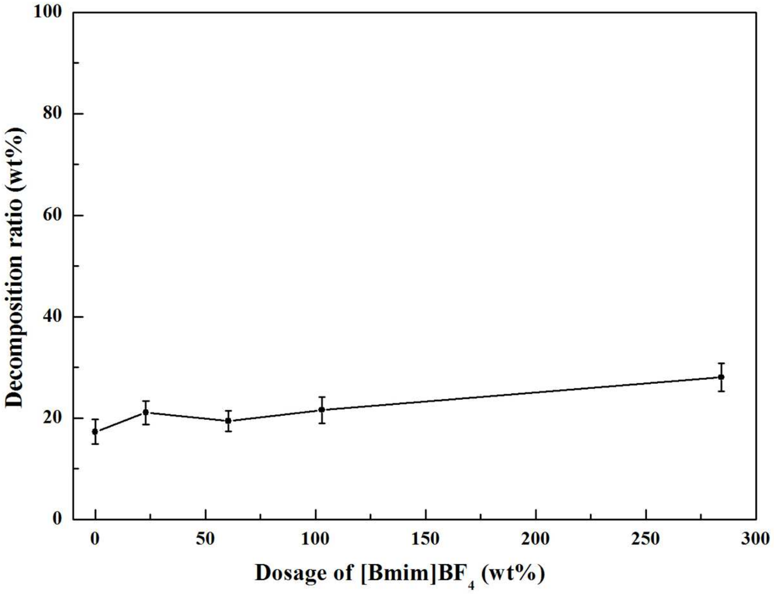


Fig. 4 The effect of [Bmim]BF4 dosage on decomposition ratio of E-51/MeTHPA system
297x209mm (150 x 150 DPI)

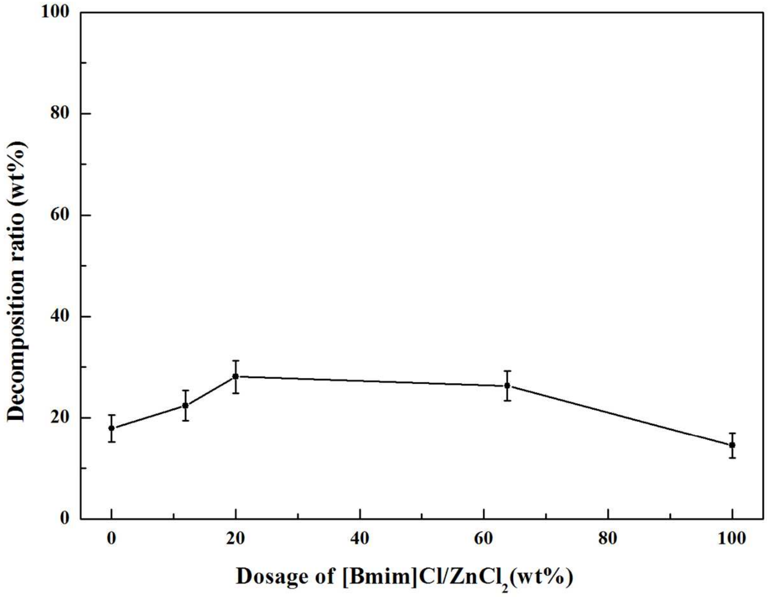


Fig. 5 The effect of [Bmim]Cl/xZnCl2 dosage on decomposition ratio of E-51/MeTHPA system
297x209mm (150 x 150 DPI)

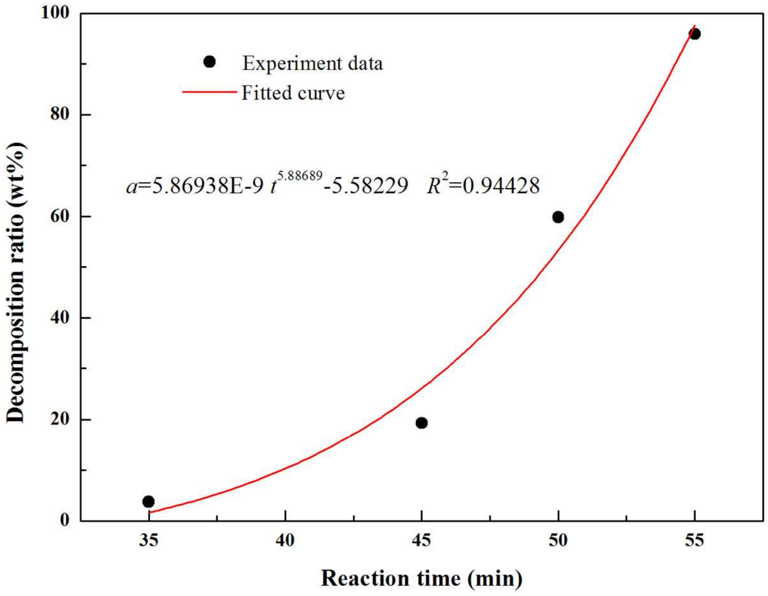


Fig. 6 The effect of reaction time on decomposition ratio without ILs (270℃)
297x209mm (150 x 150 DPI)

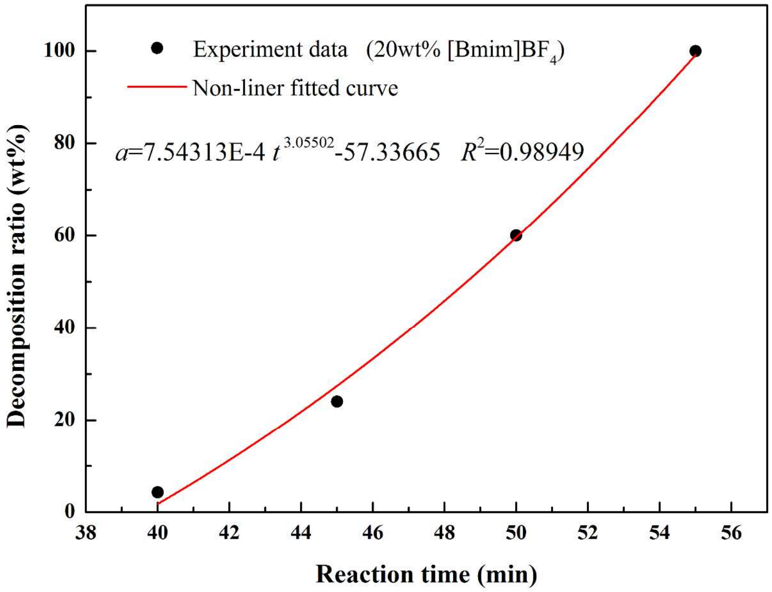


Fig. 7 The effect of reaction time on decomposition ratio with 20wt%[Bmim]BF4 (270℃)
296x209mm (300 x 300 DPI)

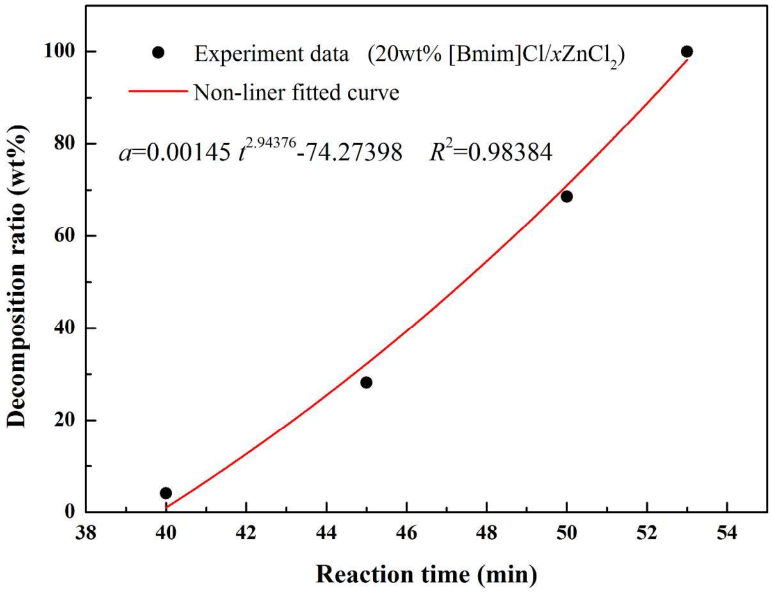
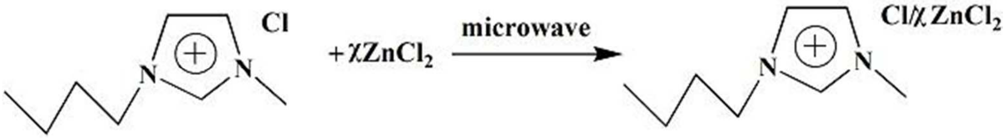
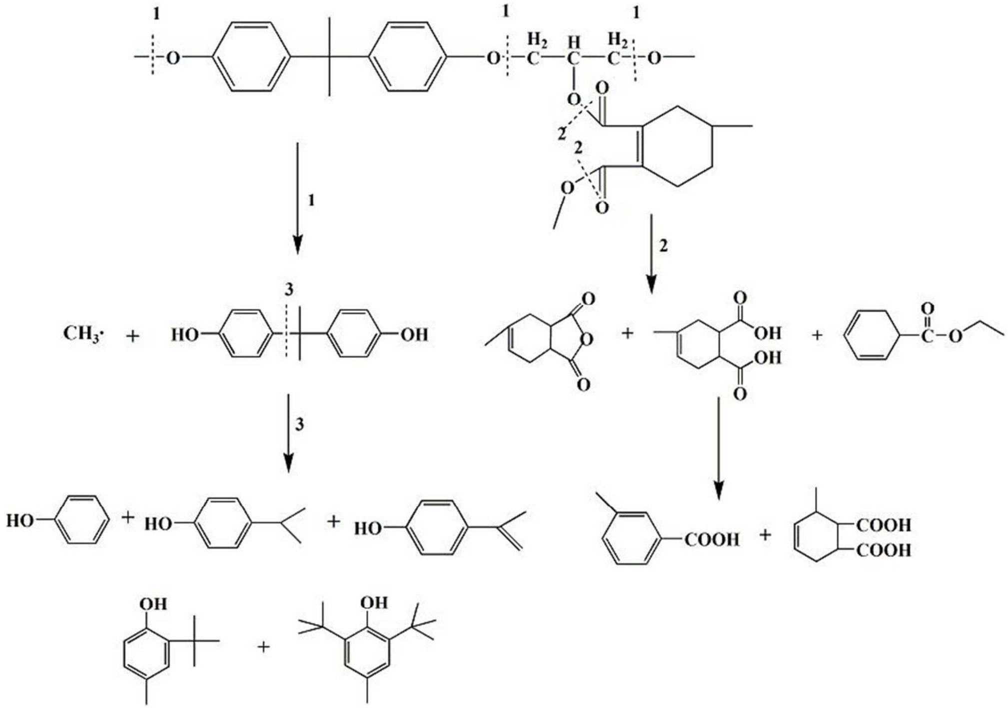


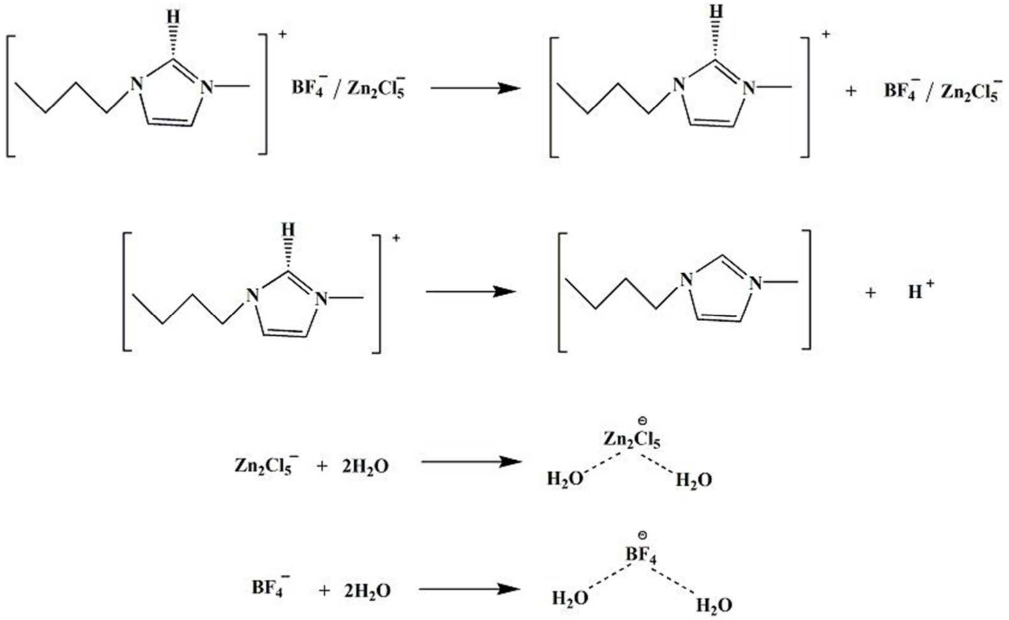
Fig. 8 The effect of reaction time on decomposition ratio with 20wt%[Bmim]Cl/xZnCl2 (270℃)
296x209mm (300 x 300 DPI)



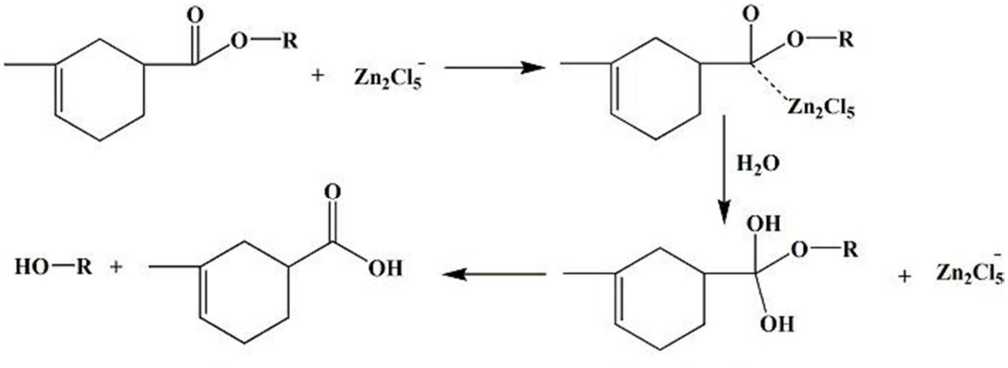
Scheme.1 The prepared route of ionic liquid [Bmim]Cl/xZnCl2
177x24mm (96 x 96 DPI)



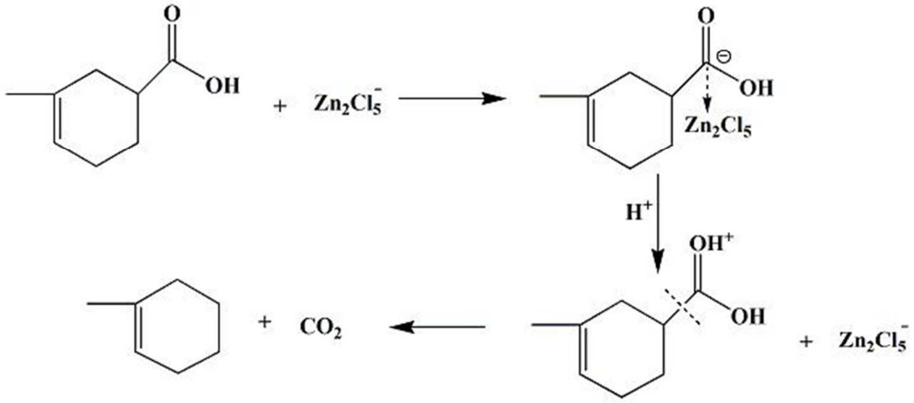
Scheme.2 The decomposition process of E-51/MeTHPA system in subcritical water
232x163mm (96 x 96 DPI)



Scheme.3 The ionization of [Bmim]BF4 and [Bmim]Cl/xZnCl2 and interaction with H2O
220x137mm (96 x 96 DPI)



(1) The fracture mechanism of ester bond with $ZnCl_2^-$ catalysis



(2) The decarboxylic reaction with $ZnCl_2^-$ catalysis

Scheme.4 The catalytic decomposition reaction of Zn2Cl5－in subcritical water
186x163mm (96 x 96 DPI)