RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances
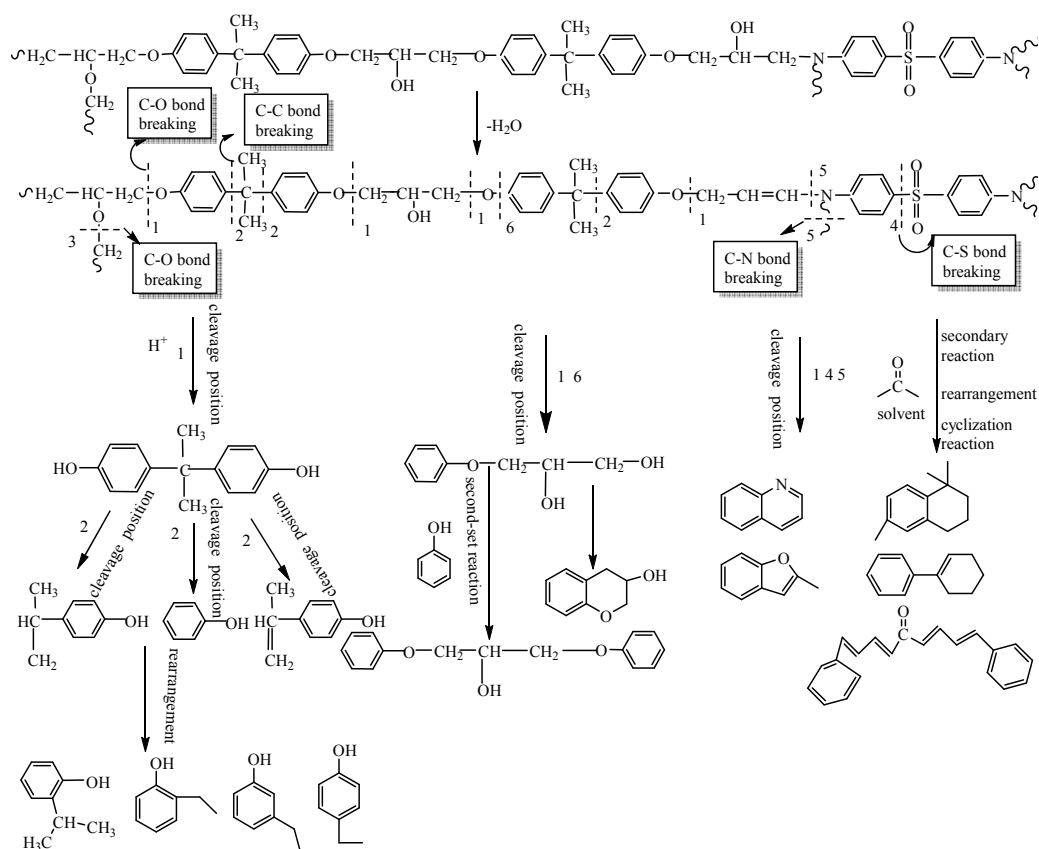
Scheme.2 Possible decomposition mechanism of the DGBFA/DDS system in near-critical water

A reaction mechanism based on the near-critical water homolysis of bonds in the polymer followed by the saturation of the resulting radicals by hydrogen abstraction from the donor was discussed. Based on the observed information, a probable macroscopic mechanism was proposed.

Decomposition Mechanisms and Kinetics of Amine/Anhydride-cured DGEBA Epoxy Resin in Near-Critical Water

Xianyun Gong[a,b], Hongjun Kang[a], Yuyan Liu[a*] and Songquan Wu[a*]

[a]*School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China*

[b]*School of Science, Department of Chemistry, Harbin University, Harbin 150086, China*

*Author to whom correspondence should be addressed

Corresponding Author: Fax: +86-0451-86413711; Tel: +86-0451-86413711;

E-mail: liuyy@hit.edu.cn (Yuyan Liu), wusongquan@hit.edu.cn (Songquan Wu)

1

Abstract: The decomposition behaviour of diglycidylether of bisphenol A (DGEBA) cured with 4-methyl tetrahydrophthalic anhydride (MeHHPA) or dapsone (DDS) in near-critical water was investigated. Reaction mechanisms based homolysis of bonds in the polymer followed by the saturation of the resulting radicals by hydrogen abstraction from the water was discussed. The decomposition rate increased with the increase of reaction time and temperature. Due to the presence of ester groups in DGEBA/MeHHPA/BDMA main chains, they were broken at the beginning of decomposition process, while it was more difficult to decompose DGEBA/DDS system, due to the introduced benzene ring. The GC-MS proved that the two resin systems were decomposed to small molecular compounds. The experimental results indicated that decomposition mechanisms of the two resin systems might involve cyclization reaction and chain-end scission in near-critical water. The two resin systems tended to form oligomers with longer molecular chain at lower temperature with the random scission. Meanwhile, a first-order kinetic model was implemented to the decomposition reaction process. The results showed that the calculated activation energy (E_a) of two resin systems was 266.7 KJ/mol and 170.7 KJ/mol, respectively.

2

1. Introduction

In recent years, thermosetting materials, epoxy resins, have widely applied in the field of electric appliances, automobile electronic and advanced composite materials,[1] due to its excellent performances, and the average annual growth rate remained above 30%. In the USA and Europe, 3000 tons of carbon fiber reinforced plastics (CFRP) wastes are generated every year, and this number is expected to rise dramatically as it is predicted that almost 6000 and 8000 airplanes containing large quantities of carbon fiber materials will reach their end-of-service life by 2030,[2] which will become an important source of waste thermosetting materials. Therefore, from the viewpoint of environment and energy saving, the recovery of waste thermosetting materials is becoming a very important issue. However, these waste materials are insoluble and infusible and they are difficult to dispose, because of their crosslinked network structures. Near-critical water (NCW, temperature at 250℃-350℃) or supercritical water (SCW) are considered as a potential media for the recycling of fibers and resin, since water is classed as a cost-effective, recyclable, non-toxic, available and green reaction media.[3-5]

In the near-critical water condition, the pH-value of water decreases by 3 units, providing much more hydronium ions for acid catalysis reactions. Just below critical temperature, the ionic product changes tremendously, rendering near critical and supercritical water a much less polar compound than ambient water. Reactivity of water increases in the neighborhood of the critical point without as well as with a catalyst.[6] Decomposition of glycerol in near critical and super critical water was investigated in a plug-flow reactor at 349-475℃, 25-45MPa, and reaction times ranged from 32s to l65s at different initial concentrations. Conversion between 0.4% and 31% was observed.[7] Recent studies on solvo-thermal recycling of CFRP have shown promising

results; as the waste can be decomposed into smaller molecules and fibre material. Solvolytic

processes such as glycolysis[8] or hydrogenolysis[9] can decompose the epoxy resin into its original

monomers to produce a potential chemical feedstock. Nitric acid solutions at 343 K-363K can

act as a reactive medium by decomposing bisphenol-F epoxy resins recovering clean carbon

fibres.[10] Eyup Yildirir et al[11] studied a solvolysis process to depolymerize the resin fraction of

carbon fibre reinforced plastic waste to recover carbon fibre, followed by hydrothermal

gasification of the liquid residual product to produce fuel gas, which was carried out in ethylene

glycol and ethylene glycol/water mixtures at near-critical conditions of the two solvents. Mingfei

Xing[12] developed an effective and benign process using sub- and supercritical water (sub/SCW)

to simultaneously degrade brominated epoxy resin and recover metals from WPCBs. Although

extensive research has been performed on the decomposition of epoxy resins, there are a few of

the literature on the decomposition mechanism and kinetics of the different cured epoxy resin

systems in near-critical water. Formerly, Kiran and WOO for polymer composites[13] and Lattimer

for five polyolefins[14] reported that a chain-end scission caused by an intramolecular radical

transfer played an important role for the production of volatile which investigated the thermal

degradation of synthesized polymers. Furthermore, Grimbley and Lehrle proposed that

polyisobutylene thermally degraded by parallel depropagation with random scission.[15] Lidia

Gonzalez[16] investigated that ester groups were thermally cleavable by a β-elimination

mechanism, which led to the formation of acid and vinyl ether groups as chain ends. Tertiary

esters are more easily thermal decomposition than primary or secondary ones. Yan Liu[17] used the

combination of phenol and potassium hydroxide (KOH) to chemically recycle carbon fibre

reinforced epoxy resin cured with 4, 4'-diaminodiphenylmethane in subcritical water, and a

possible free-radical reaction mechanism for the decomposition of epoxy resin was proposed. W.

Buhler[18] reported that the decomposition of glycerol in near-and supercritical water underwent two competing reaction pathways. One pathway consists of ionic reaction steps, which are preferred at lower temperatures. In the second reaction pathway, free radical decomposition dominated at higher temperatures. For reaction model, both the ionic and the free radical reaction mechanisms are compiled into one reaction model. Géraldine Oliveux et al[19] used hydrolysis in batch conditions to recycle composite materials reinforced with long glass fibers in subcritical water. The hydrolysis kinetics was thus defined for three widespread commercial resins and showed a good fit to the experimental data. Secondary reactions like decarboxylation of carboxylic acid and dehydration of glycol were also described in terms of mechanisms and kinetics. Pi~nero-Hernanz et al[20] studied the chemical recycling of CFRP in sub- and supercritical water. A second-order kinetic equation was implemented to model the reactive extraction process. Liu et al[21] introduced that kinetics study of the epoxy decomposition was also carried out by monitoring the glass transition temperature of the solid product. The decomposition equation was established and the activation energy was calculated to be 123.5 kJ/ mol.

In this paper, the decomposition behaviour of diglycidylether of bisphenol A (DGEBA) cured with 4-methyl tetrahydrophthalic anhydride (MeHHPA) or dapsone (DDS) in near-critical water was investigated. The effects of temperature on decomposition rate of DGEBA/MeHHPA/BDMA and DGEBA/DDS systems were studied in detail. The liquid decomposition products of the two epoxy resin systems were also analyzed. Furthermore, the possible decomposition mechanisms were proposed for DGEBA/MeHHPA/BDMA and DGEBA/DDS systems. Meanwhile, a first kinetic equation model was applied to the two epoxy resin systems and the activation energy was calculated.

2. Experimental

2.1 Materials

Commercial diglycidyl ether of bisphenol A (DGBEA) was supplied by Wuxi Resin Factory, China. The curing agent, 4-Methyl Tetrahydrophthalic Anhydride (MeHHPA), dapsone (DDS) and the accelerant, benzyl dimethylamine (BDMA), were purchased from business agents. The formed three-dimensional network structures of DGEBA/MeHHPA/BDMA and DGEBA/DDS systems are illustrated in Fig. 1 and Fig. 2, respectively.

Fig. 1

Fig. 1 The formed three-dimensional network structures of DGEBA/MeHHPA/BDMA system

Fig. 2

Fig. 2 The formed three-dimensional network structures of DGEBA/DDS system

2.2 Preparation of DGEBA/MeHHPA/BDMA and DGEBA/DDS samples

The perparation of DGBEA/MeHHPA/BDMA sample was as follows: diglycidyl ether of bisphenol A (DGBEA), curing agent (MeHHPA) and accelerant (BDMA) were mixed according to a mass ratio of 100:85.7:1 and then the mixture was poured into an iron mould. The system of DGBEA/MeHHPA/BDMA was cured at 120℃ for 5h and then heated to 150℃ for 15h.

Similarly, the perparation of DGBEA/DDS sample was as follows: diglycidyl ether of bisphenol A (DGBEA) and curing agent (DDS) were mixed according to a mass ratio of 100:34.8 and the mixture was cured at 90℃ for 4h, 120℃ for 2h, 160℃ for 6h and finally was heated to 200℃ for 6h.

It was proved that the two epoxy resin systems were cured completely by using DSC. These Finally, these cured samples were cut into cubic samples with size of 20mm×20mm×2mm and

washed with pure de-ionized water.

2.3 Decomposition process of the two epoxy resin samples

The decomposition of epoxy resins was conducted in a 100 mL stainless steel autoclave. 1 g of samples and 10 mL distilled water were employed in the reactor. Then the reactor was sealed and placed into a round salt bath furnace with a temperature controller. The reaction condition of DGEBA/MeHHPA/BDMA system was as follows: at 260℃, 265℃, 270℃, 275℃, 280℃ of 30, 45 and 60 min, respectively. The reaction condition of DGEBA/DDS system was at 300℃, 310℃, 320℃, 330℃ of 30, 45, 60 min, respectively. When the experiments finished, the reactor was cooled down to ambient temperature in a cold-water bath. The solid residues were immersed in acetone for 24 h, washed with distilled water and dried in a vacuum oven. The collected liquid acetone phase products presented yellowish brown with high viscosity, which were analyzed by chromatography-mass spectrometer (GC/MS). Finally, the obtained solid products were weighed to calculate the decomposition rate using the following eqn (1). The decomposition ratio was averaged with each experiment repeated two times.

$$R_d = \frac{(m_1 - m_2)}{m_1} \times 100\% \tag{1}$$

Where R_d represents the decomposition ratio, m_1 represents the mass of original resin systems and m_2 represents the mass of the dried solid residue after near-critical water treatment.

2.4 Characterization

The cured degree of DGEBA/MeHHPA/BDMA and DGEBA/DDS system was measured by DSC (TA Q200, USA). The sample was heated from 25℃ to 250℃ at the heating rate of 10℃/min under nitrogen atmosphere.

Thermo-gravimetric tests were carried out in the air atmosphere by TGA (ZRP-2Y) to study

the thermal oxidation decomposition of the two resin systems at 270℃ for 60min .

Chromatography-mass spectrometer (GC/MS, 6890NGC-5973NMS) equipped with a DB-5MS chromatographic column (30m×0.25m×0.25μm) was used to determine the composition and distribution of liquid products in acetone phase. The operating conditions were as follows: injection temperature was 280℃; the high purity helium was used as carrier gas at the flow rate of 1.0ml/min; column temperature was form 50℃ to 280℃; Ion source temperature was 230℃. The warming parameters were as follows: heating rate was 10℃/min in the range of 50-180℃; heating rate was 20℃/min in the range of 180-280℃. The scanning range of MS was 0-500amu and electron bombardment source was 70eV.

Dynamic mechanical analysis (DMA, SDTA861e, Mettler-Toledo) was carried out under a shear mode over a temperature range from 25℃ to 150℃ at a heating rate of 3℃/min with frequency of 1 Hz, an amplitude of 3μm, a force of 5 N, and the sample size of $10\times10\times2$ mm^3.

3. Results and discussion

3.1 Effect of temperature on decomposition rate of two epoxy resin systems

The temperature played a critical role in decomposition process. The decomposition reactions were conducted at temperatures ranging from 260℃ to 280℃ for 30, 45 and 60 min, respectively. The effect of temperature on decomposition rate of DGEBA/MeHHPA/BDMA system at different reaction time was shown in Fig. 3. It could be clearly seen that decomposition rate of DGEBA/MeHHPA/BDMA system was improved at higher temperature. With the increase of reaction temperature from 260℃ to 280℃, the decomposition rate increased from 0.020 wt% to 17.7wt% at 30 min, from 5.5 wt% to 88.9wt% at 45 min, and from 30.7 wt% to 100wt% at 60 min, respectively. When the temperature was below 265℃, the decomposition

process followed the diffusion-controlled mechanism. With distilled water diffusing into the epoxy resin, little external decomposition reaction happened. The damage degree of network structure was low and the decomposition rate was relatively low. While the temperature was among 265℃-270℃ for 60min, decomposition process was quite rapid. Afterwards, decomposition process began to slow down at above 270℃. The decomposition rate of DGEBA/MeHHPA/BDMA system reached 100wt% after 60 min at 275℃, indicating that it was decomposed completely.

Fig. 3

Fig. 3 Decomposition rate of DGEBA/MeHHPA/BDMA system *vs.* temperature in different reaction time.

For the DGEBA/DDS system, the decomposition rate was studied at 300℃, 310℃, 320℃, 330℃, 340℃ for 30, 45 and 60 min, respectively. Fig. 4 presents the effect of temperature on decomposition rate of DGEBA/DDS system at different reaction time. As shown in Fig. 4, the decomposition rate did not show the significant saltation. Because the structure of dapsone (DDS) contained many active hydrogens, the complex degree of cross-linked network structure increased. Furthermore, the introduced benzene ring could not only increase the rigidity of the molecular chain, but also non-polar of molecules, which reduced the hygroscopicity of DGEBA/DDS system and the diffusion process of water weakened in the resin system. Therefore, the decomposition of DGEBA/DDS system mainly resulted from pyrolysis effect and the decomposition rate presented the trend of linear growth. Meanwhile, it could be found that with the increase of reaction temperature from 300℃ to 340℃, the decomposition rate of DGEBA/DDS system increased from 29.2 wt% to 78.45wt% at 30 min, from 40.4 wt% to 86.1wt% at 45 min and from 44.9 wt% to 100wt% at 60 min, respectively. When the temperature reached 310℃, the surface of DGEBA/DDS sample was damaged with more cracks and the

9

color of sample went black, indicating that the carbonation reaction happened.

Fig. 4

Fig. 4 Decomposition rate of DGEBA/DDS system *vs*. temperature at different reaction time.

In conclusion, the above results showed that high temperature benefited the decomposition of the two epoxy resin systems form two effects. The first effect was the decreased water viscosity, which could increase the reacting substance diffusion and improve the decomposition rate of resin systems. The second was the dissociation of water, which could provide more H^+ and OH^- to participate in the decomposition reaction.

3.2 Thermo-gravimetric analysis of two epoxy resin systems

In order to study the influence of the thermal oxidation decomposition on the DGEBA /MeHHPA/BDMA and DGEBA/DDS systems, respectively, thermo-gravimetric tests were carried out in the air atmosphere. The thermo-gravimetric curves of DGEBA/MeHHPA/BDMA system at 270℃ for 60 min are shown in Fig. 5.

Fig. 5

Fig. 5 The thermo-gravimetric curve of DGEBA/MeHHPA/BDMA system at 270℃ for 60 min

As could be seen from Fig. 4, it was clear that DGEBA/MeHHPA/BDMA system began to loss weight at about 8 min and the descent part of the curve was smooth, indicating that the weight loss of the DGEBA/MeHHPA/BDMA system was quite little (<5%) in the process of heat treatment for 60 min. So, the decomposition of DGEBA/MeHHPA/BDMA system was attributed to near critical water treatment and the decomposition rate could reach almost 93%.

Fig. 6 shows the thermo-gravimetric curve of DGEBA/DDS system at 310℃ for 60 min. It could be clearly seen that in the beginning, the curve was relatively flat with a small amount of weight loss and thermal weight loss was only about 11% in the process of heat treatment for

60min. Therefore, the decomposition rate of DGEBA/DDS system was only 68% in near critical

water treatment process. These results indicated that the thermal decomposition played an

important role in DGEBA/DDS system at relatively higher temperature.

Fig. 6
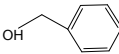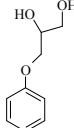
Fig. 6 The thermo-gravimetric curve of DGEBA/DDS system at 310℃ for 60 min

3.3 GC/MS analysis of liquid phase decomposition products

To know the main components of liquid phase products generated in the decomposition and

determine whether these products could be used as a source of chemicals and recovered the high

concentration or high value compounds. Therefore, the liquid decomposition products of the two

epoxy resin systems in acetone phase were analyzed to determine their compositions by using

GC/MS analysis. The results were shown in tables 1-6, respectively.

3.3.1 Product analysis of DGEBA/MeHHPA/BDMA system

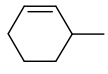Table. 1 Decomposition products of DGEBA/MeHHPA/BDMA system in cetone phase (260℃, 60 min).

Number	Retention Time (min)	Components	Structure	Relative area (%)
1	5.64	Phenol		8.65
2	6.41	Phemethylol		4.25
3	11.18	4-methyl-cyclohexene		59.11
4	11.96	3-phenoxy-1,2-propanediol		10.95

11
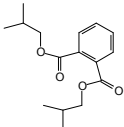
| 5 | 13.32 | Diisobutyl phthalate | | 4.15 |

Table. 2 Decomposition products of DGEBA/MeHHPA/BDMA system in cetone phase (270℃, 60 min).
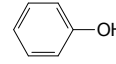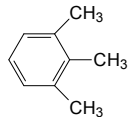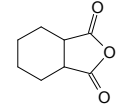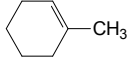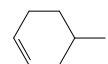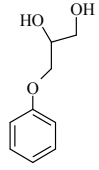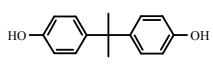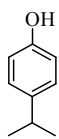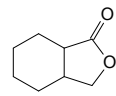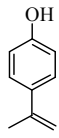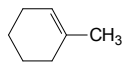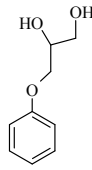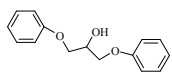
Number	Retention Time (min)	Components	Structure	Relative area (%)
1	5.42	*m*-Xylene		0.35
2	6.47	Phenol		3.72
3	6.88	1,2,3-trimethylbenzene		0.28
4	9.65	Hexahydrophthalic anhydride		7.12
5	10.10	1-methyl-1-cyclohexene		23.59
6	10.13	4-methyl-1-cyclohexene		12.61
7	11.72	3-phenoxy-1,2-propanediol		6.01
8	12.83	2H-1-benzopyran-3,4-dihydro		7.34
9	14.48	Bisphenol A		0.98

12

Table. 3 Decomposition products of DGEBA/MeHHPA/BDMA system in cetone phase (280℃, 60 min)

Number	Retention Time (min)	Components	Structure	Relative area (%)
1	4.93	Phenol		2.52
2	8.92	*p*-isopropylphenol		0.79
3	9.98	*cis*-hexahydrohydroxy phthalide		0.69
4	10.11	4-isopropenylphenol		0.56
5	10.72	Cyclohexene		2.61
6	11.31	3-methyl- cyclohexene		7.98
7	11.62	1-methyl- cyclohexene		3.87
8	12.65	3-phenoxy-1,2-propanediol		29.27
9	18.46	1,3-diphenoxy-2-propanol		1.09

Tables 1-3 show the liquid products components of DGEBA/MeHHPA/BDMA system after

60 min at temperatures of 260℃, 270℃ and 280℃, respectively. From table.1 to table. 3, it

13

could be clearly found that the relative peak area of methyl-cyclohexene compound in the liquid decomposition products decreased from 59% to 12% with the increase of temperatures from 260℃ to 280℃, which could be explained that ester groups in the main chain generated the large-scale fracture and   methyl-cyclohexene was converted   into other substances. The relative peak area of 3-phenoxy-1,2-propanediol compound increased from 10.9% to 29.2%, which might be attributed to large-scale hydrolysis of the mixed ether bonds and ester bonds in the main chain. The relative peak area of phenol compound decreased from 8.6% to 2.5%, because secondary reaction of 3-phenoxy-1, 2-propanediol and phenol happened.

At temperatures of 280℃, not only ester groups but also ether groups and C-C bond were broken. As shown in table. 3, there were a lot of new substances generated, such as *p*-isopropylphenol, 4-isopropenylphenol and so on. Furthermore, bisphenol A was decomposed to 4-isopropylphenol under hydrogenation conditions, while 4-isopropylphenol preferred to translate into 4-isopropenylphenol because of hydrogenation of 4-isopropenylphenol, which meaned that ester groups were broken much easier than ether or carbon-carbon bond. The carboxy radical could be saturated by hydrogenation or it could undergo decarboxylation, which formed methyl cyclohexene. The thermally unstable ester bonds were broken at high temperatures, forming carboxylic acid. Some of carboxylic acid groups were further translated into anhydrides in the decomposition process.

On the above basis, the decomposition reaction mechanism of DGEBA/MeHHPA/BDMA system was proposed in Scheme. 1. The elimination of water from the secondary alcohol group was the first reaction when the epoxy resin system was heated.[9] The resulted allylic bonds and aromatic ether bonds experienced homolytic cleavage.

Scheme.1

Scheme.1 Possible decomposition mechanism of DGBFA/MeHHPA/BDMA system in near-critical water.

3.3.2 Product analysis of DGEBA/DDS system

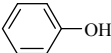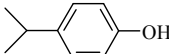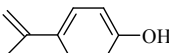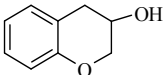Table. 4　Decomposition products of DGEBA/DDS system in acetone phase (310℃, 45 min).
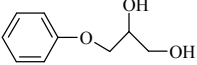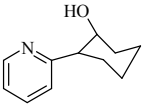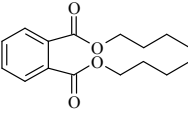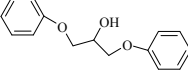
Number	Retention Time(min)	Components	Structure	Relative area (%)
1	6.74	Phenol		22.43
2	8.79	*p*-isopropylphenol		19.18
3	9.62	*p*-isopropenylphenol		2.37
4	10.08	2H-1-benzopyran-3-ol, 3,4-dihydro-		2.19
5	10.84	3-phenoxy-1,2-propanediol		17.77
6	12. 79	2-[2-pyridyl]-cyclohexanol		3.72
7	13.16	Dibutyl phthalate		1.74
8	13.71	1,3-diphenoxy-2-propanol		1.96

Table. 5 Decomposition products of DGEBA/DDS system in acetone phase (320℃, 45 min).

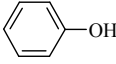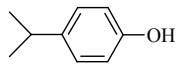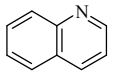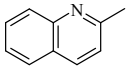| Number	Retention Time (min)	Components	Structure	Relative area (%)
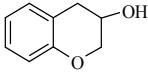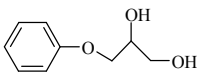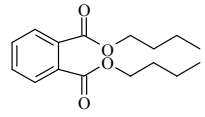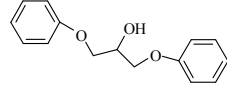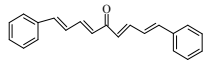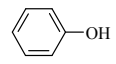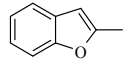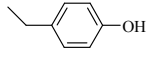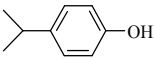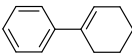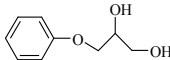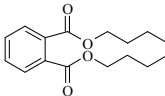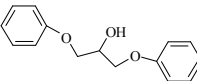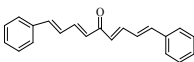
1	6.80	Phenol		21.41
2	8.83	*p*-isopropylphenol		16.12
3	9.11	Quinoline		4.29
4	9.64	2-methyl-quinoline		2.06
5	10.03	2H-1-benzopyran-3-ol,3,4-dihydro-		2.72
6	10.82	3-phenoxy-1,2-propanediol		13.70
7	13.15	Dibutyl phthalate		1.42
8	13.68	1,3-diphenoxy-2-propanol		3.14
9	14.83	1,9-diphenyl-1,3,6,8-Nonatetraen-5 -one		2.71

Table. 6 Decomposition products of DGEBA/DDS system in acetone phase (330℃, 45 min).

Number	Retention Time (min)	Components	Structure	Relative area (%)
1	6.77	Phenol		22.13
2	7.78	2-methyl-benzofuran		1.43
3	8.48	4-ethyl- phenol		0.669

4	8.61	2-(1-methylethyl)- Phenol		0.422
5	8.83	*p*-isopropylphenol		16.02
6	9.08	Quinoline		5.10
7	9.44	1-phenyl- cyclohexene		0.679
8	10.83	3-phenoxy-1,2-propanediol		10.74
9	13.15	Dibutyl phthalate		1.50
10	13.68	1,3-diphenoxy-2-propanol		2.50
11	14.84	1,9-diphenyl-1,3,6,8-nonatetraen-5-one		2.09

Tables 4-6 present the liquid products components of DGEBA/DDS system after 45 min at temperatures of 310℃, 320℃ and 330℃, respectively. From table. 4 to table. 6, a series of consecutive reactions happened during the decomposition process of DGEBA/DDS system. The decomposed compounds were complex and the main decomposition products were a mixture of phenols and alcohol. We could identify phenol, isopropyl phenol and alcohol, which were formed by the breakage of ether bonds in DGEBA/DDS sysrem main chain . The content of quinolines and furan increased with the increase of temperature from 310℃ to 330℃, while the content of phenols decreased from about 44% to 38% and alcohol decreased from 24% to 13% with increasing the temperature. The results showed that high temperature (pyrolysis) had the potential to enable a 'closed-loop' recycling scheme for DGEBA/DDS system. In the present

17

case, the resin system was simply unzipped to generate most monomers at high temperatures, such as quinolines and furan instead of a series of phenols and alcohol. However, the groups attached to the side of the chain were weaker than the bonds in the main chain. In such cases, the side groups had broken away from the main chain before they were broken into smaller pieces, such as the volatile products. In crosslinked epoxy resin system, the weakest bonds are the C-O bond,[22] connecting bisphenol A and epichlorohydrin, so high temperature decomposition could produce some oligomeric units or cyclize into monomers. The decomposition mechanism of DGEBA/DDS system was shown is Scheme. 2.

Scheme 2

Scheme.2 Possible decomposition mechanism of DGEBA/DDS system in near-critical water.

3.4 The calculation of crosslinking degree of two epoxy resin systems

For dynamic mechanical analysis (DMA), the prepared two resin systems satisfied the following two conditions:

(1) The systems are at a stable and high elastic state at high temperature

(2) There is less stress, only around 1%

Based on the above two points, the two resin systems were considered to follow the Hooke's law in this range, so they could be used rubber theory to calculate the crosslink degree. The calculation equation coud be given as

$$E \approx \frac{3\rho RT}{\overline{Mc}}$$

(2)

Where E is the storage modulus at T_g+50℃(MPa), ρ is the polymer density (g/cm^3), R is gas constant (J/mol·K), T is absolute temperature (K), $\overline{Mc}$ is the average relative molecular mass between crosslink networks. After translation, the equ (2) becomes

$$\frac{E}{3RT} = \frac{\rho}{\overline{Mc}} = \frac{m}{V \times \overline{Mc}} = \frac{\overline{Mc} \times N}{V \times \overline{Mc}} = \frac{N}{V}$$

$$(3)$$

Where V is unit volume (g/cm^3), m is the mass of unit volume resin (g), N is the number of

network chain in crosslinking networks, that is, the degree of crosslinking.

It is well-known that the crosslinking degree means the number of the crosslink bond per unit

volume and the greater the crosslinking degree of resin, the better the resistance to heat distortion.

Table 7 illustrates the crosslinking degree of two resin systems. As shown in table. 7, the

crosslinking degree of DGEBA/MeHHPA/BDMA and DGEBA/DDS systems was 6.5×10^{-4}

mol/cm^3 and 4.4×10^{-3} mol/cm^3, respectively. Therefore, the decomposition temperature of

DGEBA/DDS system was higher than that of DGEBA/MeHHPA/BDMA system.

Table. 7 The crosslinking degree of two resin systems

Epoxy resin system	DGEBA/MeHHPA/BDMA	DGEBA/DDS
T_g (℃)	102.2	199.38
Storage modulus(MPa) (T_g+50℃)	1.629	21.41
The degree of crosslinking (mol/cm^3)	6.5×10^{-4}	4.4×10^{-3}

3.5 Non-stationary model of the decomposition process

When epoxy resin system began to decompose, it was in a non-stationary state, which might

influence the decomposition curve. Because the solubility of reaction products in the water

medium is low, mass transfer from resin matrix to the bulk fluid is strongly limited at the

beginning. For this case, the initial period of approximate 30 min was not discussed in kinetics.

The experimental data were fitted to a kinetic model to predict the reaction rate coefficient

and Arrhenius-type equation was used to determine the decomposition activation energy of the

two resin sysytems. Assuming that the decomposition reactions of DGEBA/ MeHHPA/BDMA

and DGEBA/DDS systems conformed to a first order equation model and the reaction took place

at constant rate when the vessel reached a certain temperature.

The differential equation, which describes decomposition process of epoxy resin system, is

introduced, as shown in eqn (5) [21].

$$\frac{dW}{dT} = -k_{ef} \bullet W^n \qquad (5)$$

For the case of first-order rate of reaction:

$$\frac{dW}{dT} = -k_{ef} \bullet W \qquad (6)$$

Integrating the eqn (6):

$$ln\frac{W}{W_0} = -k_{ef} \bullet t \qquad (7)$$

Where, the "W_0" is initial mass of resins (g), the "W" is mass of some time (g)/(t), "n" is the

order of reaction and "k_{ef}" is an effective reaction rate coefficient.

After introduction of $\alpha = \dfrac{W_0 - W}{W_0}$, "$a$" is the decomposition rate for the time of t moment

and then the eqn (3) turns into eqn (4):

$$-ln(1-\alpha) = k_{ef} \bullet t \qquad (8)$$

According to the equ (8), if $-ln(1-\alpha)$ vs t at different temperatures presented a good linear

relation, the assumption of first order reaction was right and the slope of fitting straight line was

reaction rate coefficient.

The plots of $-ln(1-\alpha)$ vs t at different temperatures of DGEBA/MeHHPA/BDMA and

DGEBA/DDS systems were depicted in Fig. 7 and Fig. 8, respectively. From Fig. 7 and Fig. 8, it

was clear that the plots of $-ln(1-\alpha)$ vs t at different temperatures of the two epoxy resin systems

showed a good fit, which indicated that the assumption of first order reaction was right. Meanwhile, reaction rate constants (k_{ef}) of different temperatures were obtained by the slopes of fitting straight lines.

Fig. 7

Fig. 7 Plots of -ln(1-a) vs time (t) at different temperatures of DGEBA /MeHHPA/BDMA system

Fig. 8

Fig.8 Plots of -ln(1-a) vs time (t) at different temperatures of DGEBA /DDS system

In addition, activation energy (E_a) is an an important parameter of epoxy resin decomposition dependence on temperatures and Arrhenius equation could be describe the its quantitative rule. Taking logarithms in both sides of Arrhenius equation, it becomes

$$ln\,K_{ef} = ln\,A - \frac{E_a}{RT} \tag{9}$$

Where A is the pre-exponential factor and E_a is the activation energy.

Table. 8 presents the calculated reaction rate coefficients of DGEBA/MeHHPA/BDMA system at 533K, 538K, 543K, and 548K, respectively. As shown in table. 8, this reaction rate coefficient increased obviously with the increase of temperatures from 533K to 548K ($K_{ef(533)}$=0.019min^{-1}; $K_{ef(538)}$=0.027min^{-1}; $K_{ef(543)}$=0.083min^{-1}; $K_{ef(548)}$=0.086min^{-1}).

Table. 8 The calcuated reaction rate coefficients and Arrhenius parameters for DGEBA/ MeHHPA/BDMA system decomposition in near-critical water

	T（K）	T（K）	T（K）	T（K）
	533	538	543	548
k_{ef}（min^{-1}）	0.019	0.027	0.083	0.086
n	1	1	1	1
E_a (KJ/mol)		E_a=266.7		

21

Furthermore, linear realtion of ln lnK_{ef} *vs* 1/T of DGEBA/MeHHPA/BDMA system is presented in Fig. 9. It could be found that the fit of ln(k) *vs* 1/T of DGEBA/MeHHPA/BDMA system was good, as shown in Fig. 9 and according to Arrhenius equation, reaction apparent activation energy (E_a) was calculated to be 266.7 kJ/mol for DGEBA/MeHHPA/BDMA system.

Fig. 9

Fig. 9 Linear realtion of ln(K_{ef}) *vs* 1/T of DGEBA/MeHHPA/BDMA system

Table. 9 displays the calculated reaction rate coefficients of DGEBA/DDS system at 573K, 583K, 593K, and 603K, respectively. As shown in table. 9, it could be clearly found that these coefficients increased obviously with the increase of temperatures from 573K to 603 K ($K_{ef(573)}$=0.0089min^{-1}; $K_{ef(583)}$=0.020min^{-1}; $K_{ef(593)}$=0.036min^{-1}; $K_{ef(603)}$=0.052min^{-1}).

Table. 9 The calcuated reaction rate coefficients and Arrhenius parameters for DGEBA/DDS system decomposition in near-critical water

	T（K）	T（K）	T（K）	T（K）
	573	583	593	603
k_{ef}（min^{-1}）	0.0089	0.020	0.036	0.052
n	1	1	1	1
E_a (KJ/mol)		E_a=170.6		

Similarly, the line fitting relation of lnK_{ef} *vs* 1/T of DGEBA/DDS system was shown in Fig.10. It was clear that the fit ln K_{ef} *vs* 1/T of DGEBA/DDS system was also good. The calculated reaction apparent activation energy (E_a) was 170.6 KJ/mol for DGEBA/DDS system.

Fig. 10

Fig. 10 Linear realtion of ln ln(K_{ef}) *vs* 1/T of DGEBA/DDS system

4. Conclusion

Two epoxy resin systems of DGEBA/MeHHPA/BDMA and DGEBA/DDS were successfully decomposed in nearcritical water. Evident differences were obtained between the two systems, which could be attributed to the different chemical structure of curing agent and decomposition condition. For curing agent of MeHHPA/BDMA, new generated ester bonds of curing reaction were thermally unstable, so the decomposition temperature was relative low, while the curing agent of DDS contained rigid groups of benzene, which increased its heat resistance, so the decomposition temperature was relative high and the decomposition products were easy to occur cylization reaction and form quinolones, furan substances, etc. Their decomposition mechanisms were different.

The experimental results indicated that decomposition of the two resin systems consisted of about three distinct reactions in near-critical water, which occurred simultaneously in the reactor. The first was a random scission of links, which caused a molecular weight reduction of the original polymer, and the second was a chain-end scission of C-C bonds, which caused the generation of the volatile product. The third was a cyclization reaction, which usually happened at high temperature, so high temperature decomposition could produce smaller oligomeric units or cyclize into monomers. The reaction types were considered as follows: initiation reactions, β-elimination reaction, hydrogen transfer reactions, radical isomerizations, radical dehydratizations, radical substitutions, and radical termination reactions.

A first-order kinetic equation model was successfully applied to the decomposition reaction of the two epoxy resin systems. The activation energy values, calculated from the kinetic study, were 266.7 KJ/mol and 170.6 KJ/mol for the decomposition of DGEBA/MeHHPA/BDMA and DGEBA/DDS systems, respectively.

Acknowledgements

References

1   T. Abraham, *Chem. Eng. World.*, 1994, **29**, 31

2   P. M. Vicki, *Reinforced Plastics.,* 2010, **54**, 33.

3   M. Goto, *Supercrit. Fluids.*, 2009, **47**, 500.

4   C. Fromonteil, P. Bardelle and F. Cansell, *Ind. Eng. Chem. Res.*, 2000, **39**, 922.

5   K. Arai, R.L. Smith and T.M. Aida, *Supercrit. Fluids.*, 2009, **47**, 628

6   G. Brunner, *J. of Supercritical Fluids.,* 2009 , **47**, 373.

7   W. Bühler, E. Dinjus and H. J. Ederer, *J. of Supercritical Fluids.,* 2002, **22**, 37.

8   E. Gersifi, G. Durand and G. Tersac, *Polymer Degradation and Stability.,* 2006, **91**, 690.

9   D. Braun, W. Gentzkow and A. P. Rudolf, *Polymer Degradation and Stability.,* 2001, **74**, 25.

10   W. Dang, M. Kubouchi and S. Yamamoto, *Polymer.,* 2002, **43**, 2953.

11   E. Yildirir, J. A. Onwudili and P. T. Williams, *J. of Supercritical Fluids.,* 2014, **92**, 107.

12   M. F. Xing and F. S. Zhang, *Chemical Engineering Journal.*, 2013, **219**, 131.

13   E. M. Woo, J. S. Chen and C. S. Carter, *Polymer composites.,* 1993, **14**, 395.

14   R. P. Lattimer, *Journal of Analytical and Applied Pyrolysis.,* 1995, **31**, 203.

15   M. Grimbley and R. Lehrle, *Polymer Degradation and Stability.,* 1995, **48**,441.

16   L. Gonzalez, X. Ramis and J. M. Salla, *Polymer Degradation and Stability.,* 2007, **92**, 596.

17   Y. Liu, J. Liu and Z. W. Jiang, *Polymer Degradation and Stability.,* 2012, **97**, 214.

18   W. Bühler, E. Dinjus and H. J. Ederer, *J. of Supercritical Fluids.,* 2002, **22**, 37.

19   G. Oliveux, J. L. Bailleul. N. Lefèvre and G. Biotteau, *Composites: Part A.*, 2012, **43**, 1809.

20   R. P. Hernanz, C. Dodds. J. Hyde, S. Pickering and E. Lester, *Composites: Part A*., 2008, **39**, 454.

21   Y. Y. Liu, H. G. Wei, S. Q. Wu and Z. H. Guo, *Chem. Eng. Technol.,* 2013, **36**, 2117.

22   N. P. S, Chauhan and S. C. Ameta, *Polymer Degradation and Stability.,* 2011, **96**, 1420.

Caption

Fig. 1 The formed three-dimensional network structures of DGEBA/MeHHPA/BDMA system

Fig. 2 The formed three-dimensional network structures of DGEBA/DDS system.

Fig. 3 Decomposition rate of DGEBA/MeHHPA/BDMA system *vs*. temperature in different reaction time.

Fig. 4 Decomposition rate of DGEBA/DDS system *vs*. temperature at different reaction time.

Fig. 5 The thermo-gravimetric curve of DGEBA/MeHHPA/BDMA system at 270℃ for 60 min.

Fig. 6 The thermo-gravimetric curve of DGEBA/DDS system at 310℃ for 60 min

Fig. 7 Plots of -ln(1-*a*) vs time (*t*) at different temperatures of DGEBA /MeHHPA/BDMA system

Fig. 8 Plots of -ln(1-*a*) vs time (*t*) at different temperatures of DGEBA /DDS system

Fig. 9 Linear realtion of ln(K_{ef}) *vs* 1/T of DGEBA /MeHHPA/BDMA system.

Fig. 10 Linear realtion of ln ln(K_{ef}) *vs* 1/T of DGEBA/DDS system.

Table. 1 Decomposition products of DGEBA/MeHHPA/BDMA system in cetone phase (260℃, 60 min).

Table. 2 Decomposition products of DGEBA/MeHHPA/BDMA system in cetone phase (270℃, 60 min).

Table. 3 Decomposition products of DGEBA/MeHHPA/BDMA system in cetone phase (280℃, 60 min)

Table. 4 Decomposition products of DGEBA/DDS system in acetone phase (310℃,45 min).

Table. 5 Decomposition products of DGEBA/DDS system in acetone phase (320℃, 45 min).

Table. 6 Decomposition products of DGEBA/DDS system in acetone phase (330℃, 45 min).

Table. 7 The crosslinking degree of two resin systems

Table. 8 The calcuated reaction rate coefficients and Arrhenius parameters for DGEBA/MeHHPA/BDMA
           system decomposition in near-critical water

Table. 9 The calcuated reaction rate coefficients and Arrhenius parameters for DGEBA/DDS system
           decomposition in near-critical water

**Scheme. 1** Possible decomposition mechanism of DGEBA/MeHHPA/BDMA system in near-critical water.

Scheme. 2 Possible decomposition mechanism of DGEBA/DDS system in near-critical water.
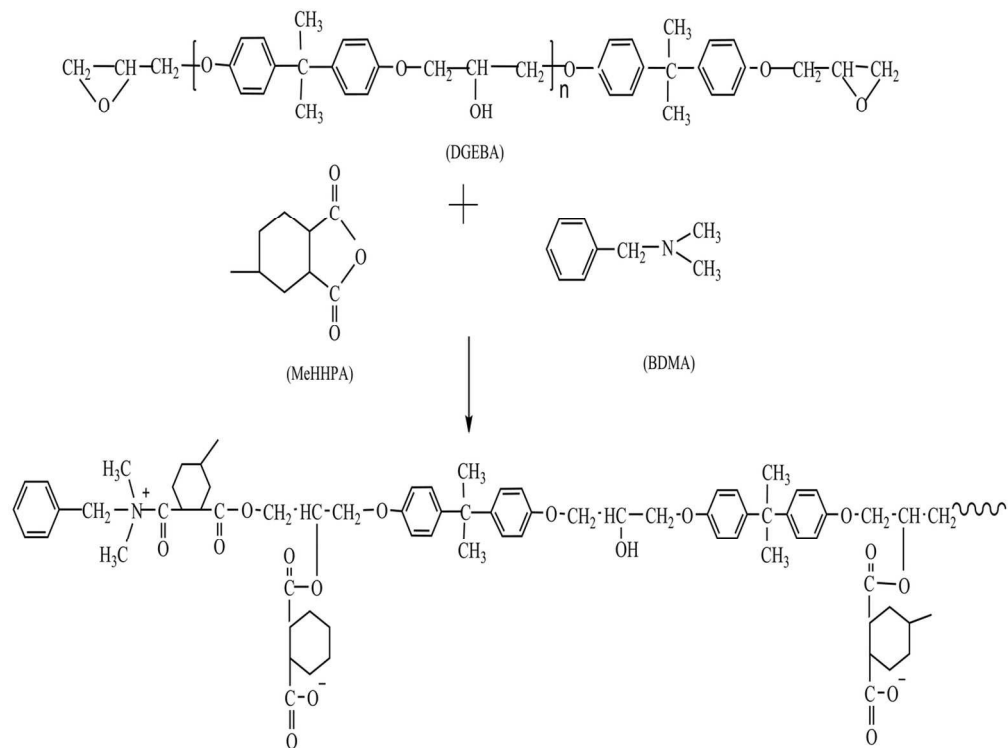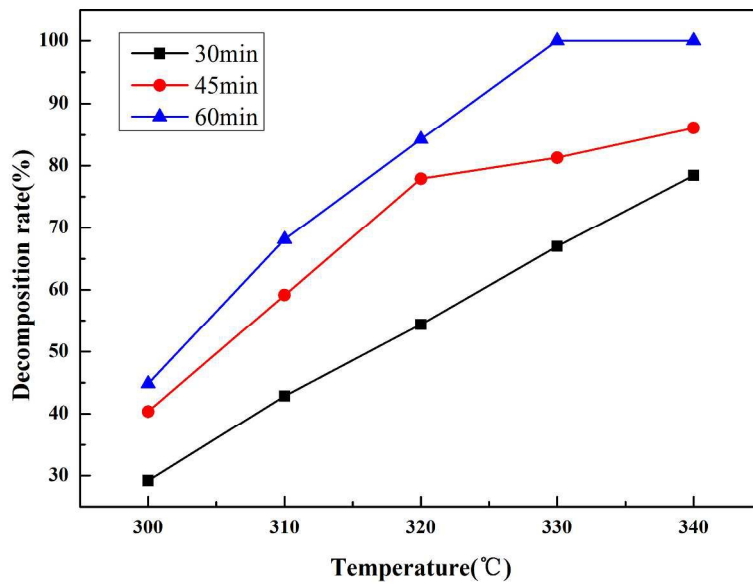
The formed three-dimensional network structures of DGEBA/MeHHPA/BDMA system
63x47mm (600 x 600 DPI)
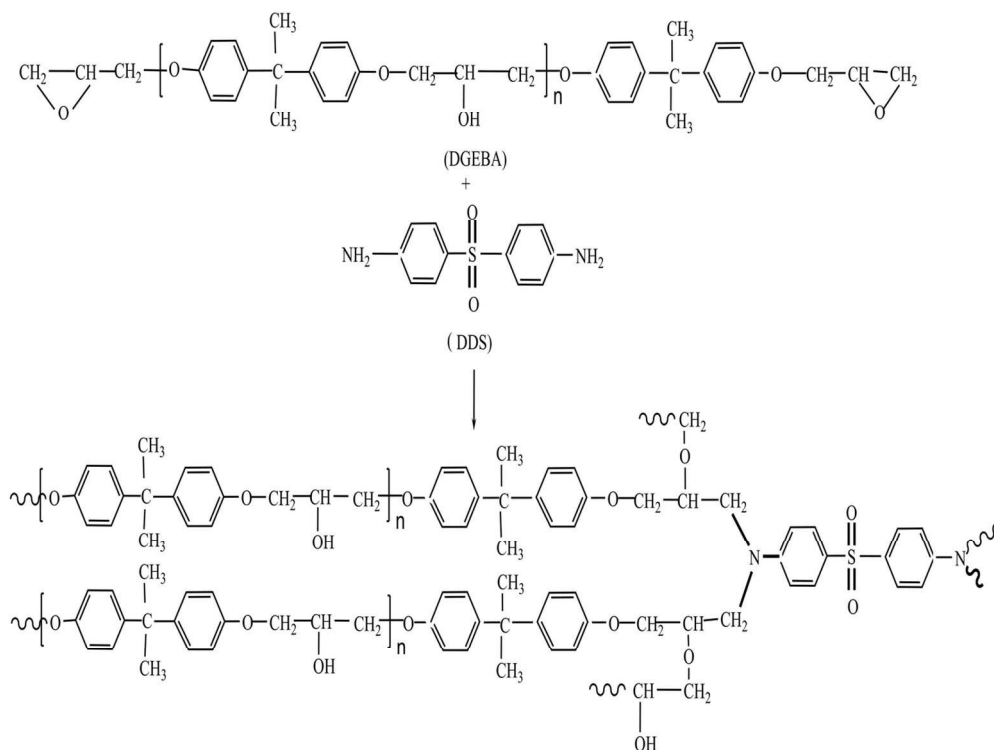
The formed three-dimensional network structures of DGEBA/DDS system.
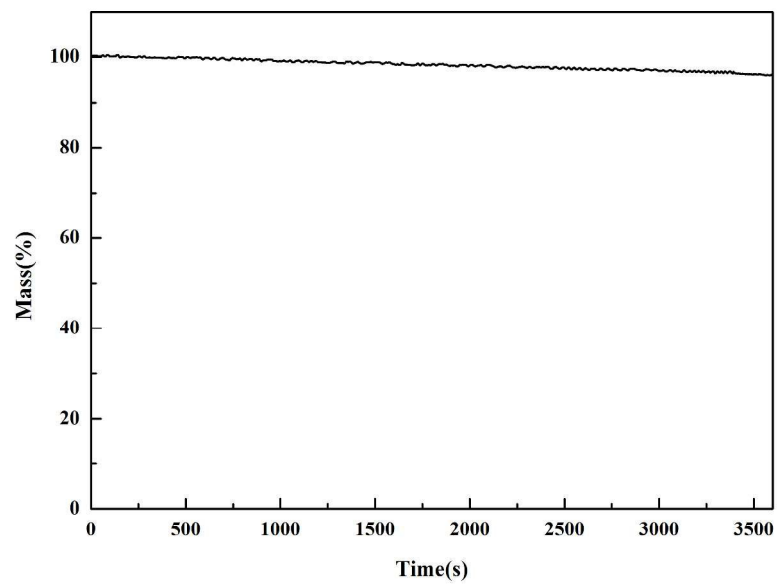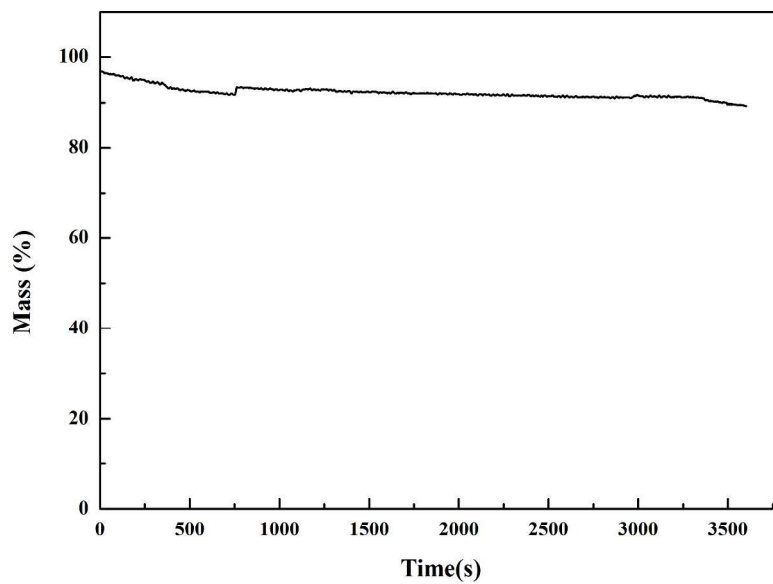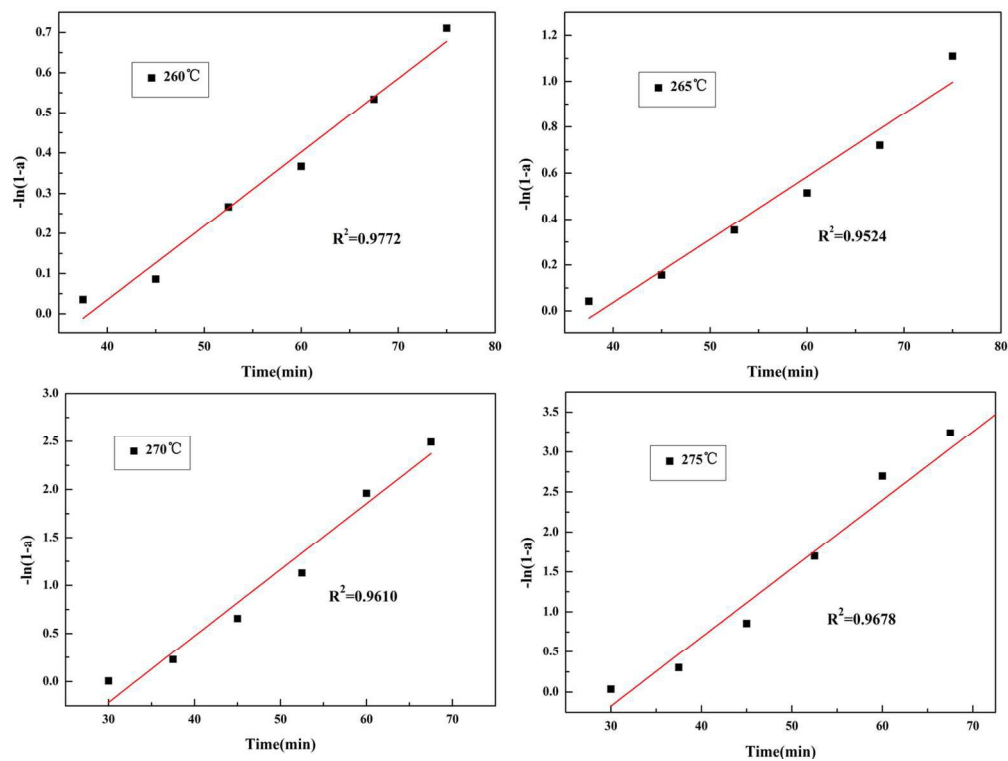63x47mm (600 x 600 DPI)
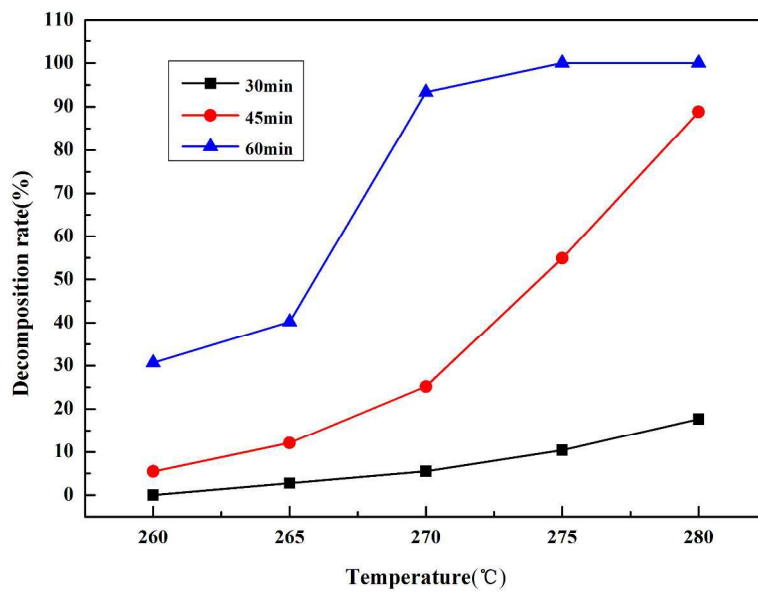
Decomposition rate of DGEBA/MeHHPA/BDMA system vs. temperature in different reaction time
285x197mm (300 x 300 DPI)

Decomposition rate of DGEBA/DDS system vs. temperature at different reaction time
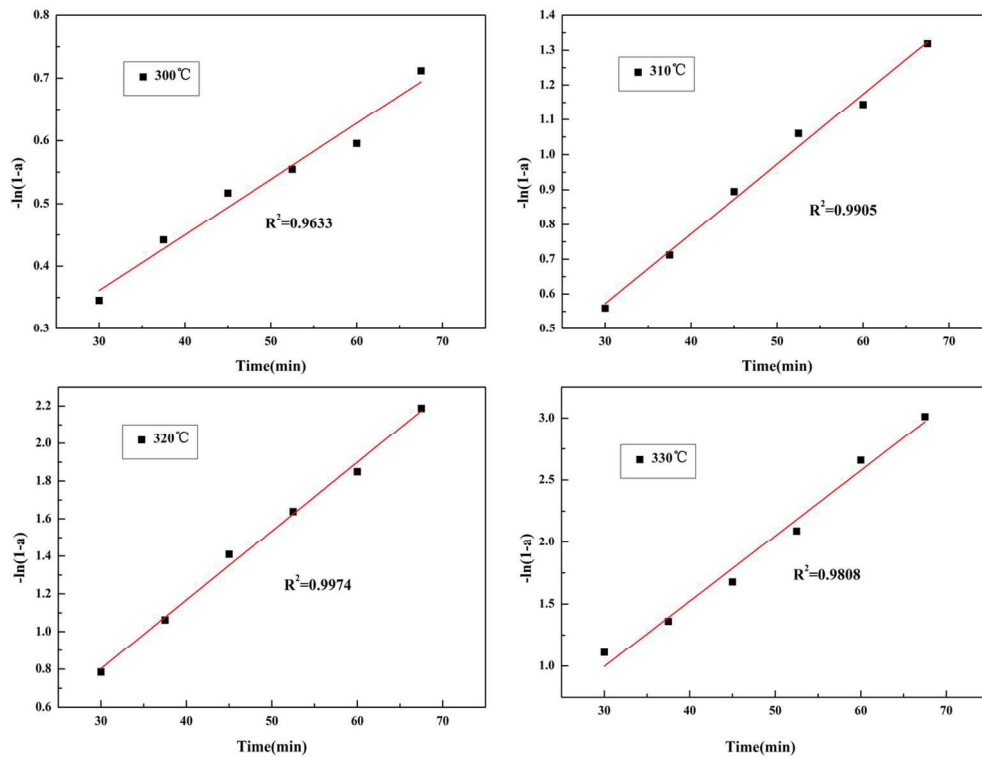285x197mm (300 x 300 DPI)

The thermo-gravimetric curve of DGEBA/MeHHPA/BDMA system at 270℃for 60 min
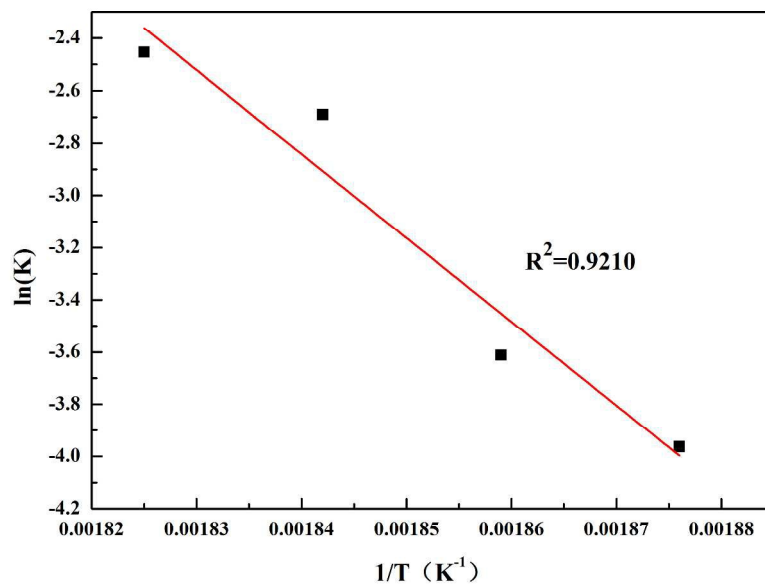285x197mm (300 x 300 DPI)

The thermo-gravimetric curve of DGEBA/DDS system at 310℃ for 60 min
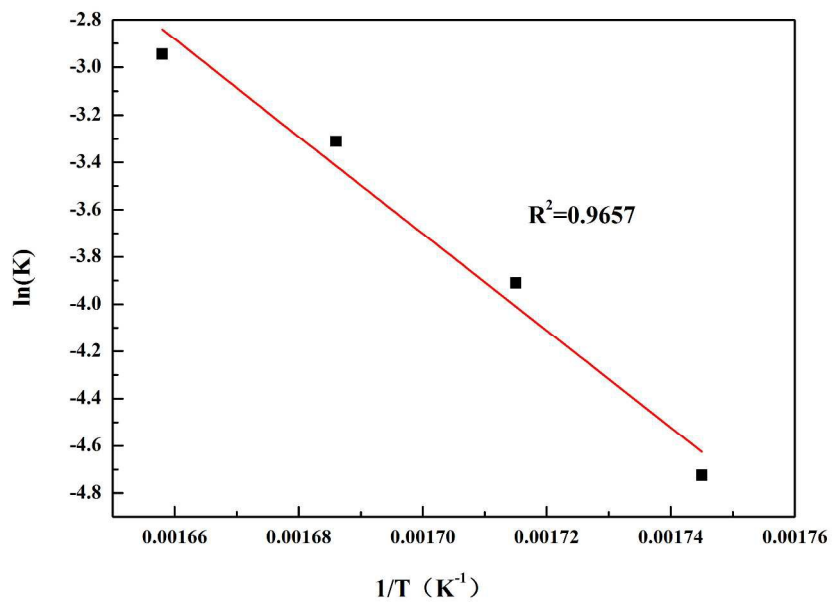285x197mm (300 x 300 DPI)

Plots of -ln(1-a) vs time (t) at different temperatures of DGEBA /MeHHPA/BDMA system
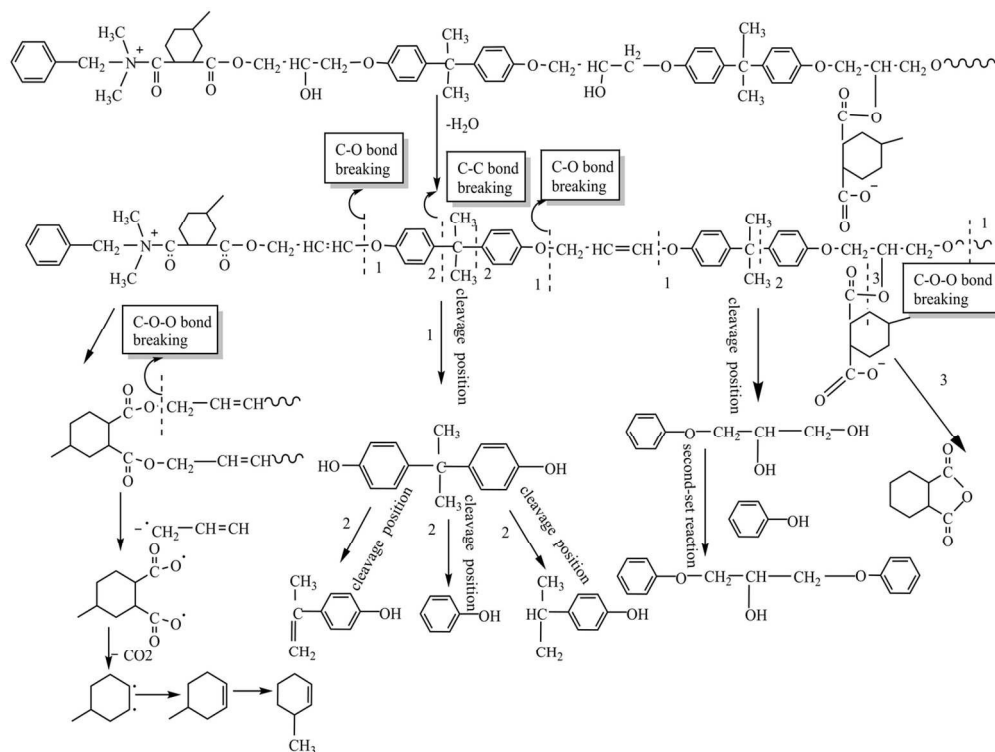63x47mm (600 x 600 DPI)

Plots of -ln(1-a) vs time (t) at different temperatures of DGEBA /DDS system
63x47mm (600 x 600 DPI)

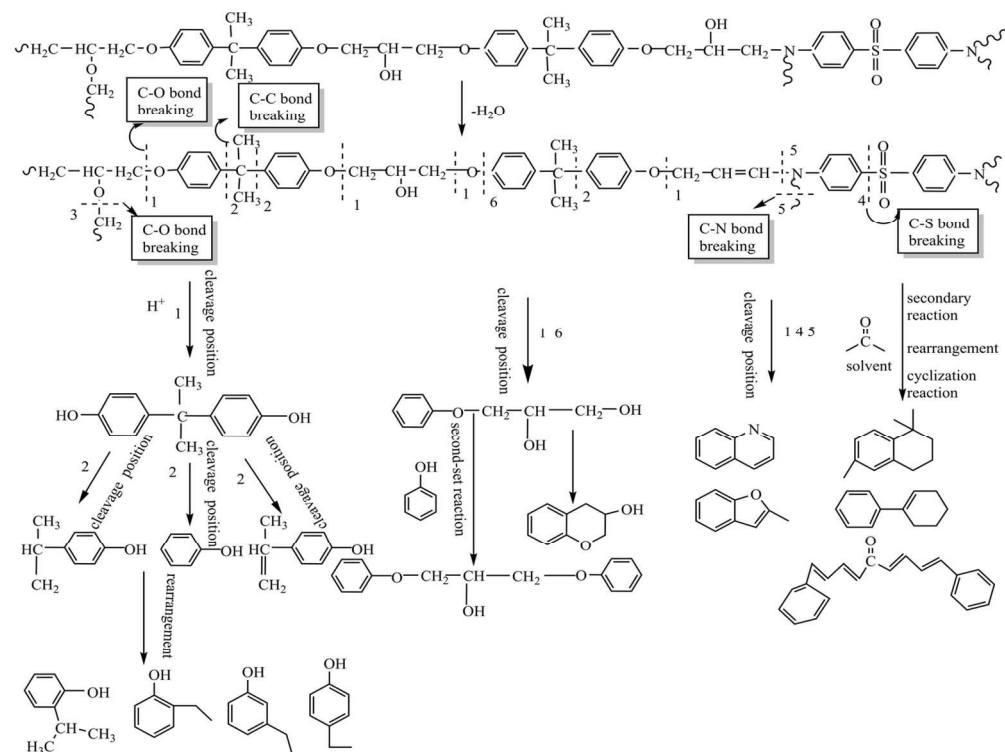Linear realtion of ln(Kef) vs 1/T of DGEBA /MeHHPA/BDMA system.
285x197mm (300 x 300 DPI)

Linear realtion of ln ln(Kef) vs 1/T of DGEBA/DDS system.
285x197mm (300 x 300 DPI)

Possible decomposition mechanism of DGEBA/MeHHPA/BDMA system in near-critical water.
63x47mm (600 x 600 DPI)

Possible decomposition mechanism of DGEBA/DDS system in near-critical water.
63x47mm (600 x 600 DPI)