

Decomposition mechanisms of cured epoxy resins in near-critical water

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ABSTRACT: A reaction mechanism based on the near-critical water homolysis of bonds in the cured epoxy followed by the saturation of the resulting radicals by hydrogen abstraction from the donor was discussed. The compounds evolved during degradation were identified by gas chromatography and mass spectrometer. The materials prepared possess the characteristics of thermosets, due to the presence of ether groups in the polymer chains, which were broken at the beginning of degradation. The degradability increased when the reaction time and reaction temperature increased. Based on the experimental results, a probable macroscopic mechanism was proposed. The near-critical water degradation mechanisms of polymers consist of three categories: random scission, unzipping, and side group elimination, which simultaneously occurs in the reactor. The first random scission of links caused a molecular weight reduction of the raw polymer, the second side-group elimination caused the generation of the volatile product, and the last unzipping produced either fragmentation to smaller oligomeric units or unzipping all the way to monomers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41648.

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INTRODUCTION

Epoxy resin thermosets received special attention owing to their remarkable stability, and higher resistance at elevated temperatures. Thermoset composite materials are used in a wide range of applications in industries such as automotives and constructions in a variety of forms. Zhu *et al.*¹ fabricated carbon nanofibers (CNFs) epoxy resin nanosuspensions and the corresponding polymer nanocomposites. Gu *et al.*² prepared epoxy resin nanocomposites reinforced with both as-received silica and polyaniline-functionalized silica nanoparticles at different loading levels. Although there are many successful uses for thermoset materials, recycling at the end of the life cycle is a more difficult issue. However, the perceived lack of recyclability is now increasingly important and seen as a key barrier to the development or even continued use of materials in some markets. The recovery of resources from thermosets wastes is becoming a very important issue from the viewpoint of environmental and energy considerations, because these materials are insoluble and infusible and they are difficult to dispose arising from their crosslinked network structures. The amount of waste plastics is increasing worldwide. The world's limited

reserve of coal, crude oil, and natural gas places a great pressure on mankind to preserve its existing nonrenewable materials.³ Waste management is now a high priority within the European Union and there is a well known hierarchy of routes for dealing with wastes. In decreasing order of desirability, these are waste minimization, reuse, recycling, incineration with energy recovery/composting, and lastly incineration without energy recovery/landfill.⁴

The widespread use of epoxy materials in technological applications is due to their excellent adhesive and thermo mechanical properties as well as their easy processing. Once cured to form highly cross-linked networks with a high thermal stability, these resins can be disadvantageous from an ecological point of view. The degradation of waste plastics into fuel represents a sustainable way for the recovery of the organic content of the polymeric wastes and also preserves valuable petroleum resources in addition to protecting the environment.^{5,6} Now it is known that high temperature and pressure water present some unique properties such as dissolution of non-polar organic, low dielectric properties, high diffusibility, and high concentrations of H⁺ and OH⁻ ions from dissociation of water. The distilled water

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ionic product ($[H]^+[OH]^-$) is 10^{-14} at 25°C , while this value increases to 10^{-11} and the concentration of $[H]^+$ reaches 3×10^{-5} mol/L at 250°C . These properties allow using water as reaction medium instead of hazardous volatile organic solvents.^{7–9} Water at temperatures higher than the ambient boiling temperature can be applied for extraction. At lower temperatures, ionic and polar species will be extracted. At higher temperatures, in particular approaching the critical temperature, nonpolar substances will be readily dissolved and extracted. A complete dissolution seems not to be a necessary. Water removes nonpolar compounds from substrate by interacting with the substrate and reducing binding forces. In such a way, hot pressurized, especially near-critical water, was applied to clean the soil, remove PAH,¹⁰ hydrocarbons, and metals. Hot pressurized water has a high reactivity. The reactions are commonly summarized as hydrolysis reactions. These are reactions in which a compound is split by water according to the equation¹¹:



Although extensive research has been performed on the decomposition of epoxy resins, there are a few of the literature on the near-critical water decomposition of different cured epoxy resin systems. Most of the previous researches on the thermal degradation of polymers have focused on the stability and/or the degradation mechanism of synthesized polymers. For example, Kiran and Gillham for PE¹² and Lattimer for five polyolefins¹³ reported that a chain-end scission caused by an intramolecular radical transfer plays an important role in producing volatile gases. Furthermore, Grimbley and Lehrle proposed that polyisobutylene was thermally degraded by parallel depropagation with random scission.¹⁴ González *et al.*¹⁵ investigated the thermal degradation mechanism of thermosetting materials prepared by cationic copolymerization of mixtures of different proportions of diglycidylether of bisphenol A (DGEBA) with 6,6-dimethyl (4,8-dioxaspiro[2.5]octane-5,7-dione) (MCP) initiated by ytterbium or lanthanum triflate. Ester groups were thermally cleavable by a β -elimination mechanism, leading to the formation of acid and vinyl ether groups as chain ends. Tertiary esters were more easily thermally degraded than primary or secondary ones. Liu *et al.*¹⁶ introduced that a diglycidyl ether type epoxy resin from bisphenol A, E-51, was cured by methylhexahydrophthalic anhydride (MeHHPA) and then decomposed in near-critical water without any additives. Liu *et al.*¹⁷ studied that decomposition mechanism of the E-51/MeTHPA cured system in near-critical water with acid–base catalysts, who thought that KOH catalyst could accelerate the breakage of ether bond of the E-51/MeTHPA system, while the breakage of ester bond was restrained, and H_2SO_4 catalyst had the same effect on the breakage of ether bond and ester bond. Chen *et al.*¹⁸ studied the thermosets incorporating a cycloaliphatic epoxy monomer that contains a tertiary ester linkage. They also studied the chemical and thermo-mechanical breakdown mechanisms of the monomer and resulting polymer networks as a function of their rework conditions. The chemical degradation mechanisms of the α -Terp epoxy monomer and the α -Terp network were found to be consistent with tertiary ester degradation mechanisms, the thermally labile tertiary ester linkage was cleaved at elevated

temperatures, thereby breaking down the polymer network and forming carboxylic acid and alkene moieties. Some of the carboxylic acid groups reacted further to form anhydrides in the breakdown process. Liu *et al.*¹⁹ studied the decomposition of epoxy model compounds, containing an ether bond and bisphenol-A structure and the other comprising ether and tertiary amine bonds in the near-critical water. The decomposition products in both model compounds were found unstable and could react with each other to generate other compounds. Decomposition mechanisms were also proposed based on the decomposition products for the model compounds. The thermal degradation process of polyesters is well documented in the literature.²⁰ However, the near-critical water degradation mechanism of epoxy resins is rarely discussed, thus the primary purpose of studying the near-critical water degradation mechanism involved in different resin and same curing agent is to confirm the mechanism as well as to establish a general procedure for studying recycling thermosets.

In this study, the author performed the near-critical water degradation of diglycidylether of bisphenol A (DGEBA)/triethylene tetramine (TETA), diglycidylether of bisphenol F (DGEBF)/triethylene tetramine (TETA), and tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM)/triethylene tetramine (TETA). Thus, the rate and the product from near-critical water degradation of those polymers were obtained in a steady state. The decomposition of three kinds of epoxy resins cured with TETA in near-critical water was investigated, analyzed, and compared. The compounds decomposition mechanism was discussed.

EXPERIMENTAL

Three kinds of epoxy resins diglycidylether of bisphenol A (DGEBA), diglycidylether of bisphenol F (DGEBF), and tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) were all cured with triethylene tetramine (TETA) at weight ratio of 100 : 13.03, 100 : 15.07, 100 : 20.44 in theory, respectively, and the epoxy value of three kinds of epoxy resins are 0.51, 0.59, and 0.80, respectively. To crosslink the samples, the mixtures were poured into an iron mold and then cured at room temperature for 48 h, followed by post-curing at 100°C for 3 h. The samples were then allowed to be cooled down to room temperature. Figure 1 shows the chemical structure of the three-dimensional polymer formed. It was confirmed by DSC that they were completely cured, Supporting Information Figure S1–S3. The samples were cut into 20 mm squares with 2-mm-thick plate and washed with pure de-ionized water.

The decomposition of epoxy resins was performed at different temperatures in an air atmosphere, unstirred in a 100 mL tube stainless steel autoclave. In a typical run, 1 g of sample measuring 2×2 cm² and 10 mL distilled water were used in the reactor directly at the same time. Then the reactor was sealed and placed into a round salt bath furnace with temperature controlling which the heating rate was $20^\circ\text{C}/\text{min}$ from room temperature to set temperature. When the experiments finished, the reactor was cooled down to ambient temperature in a cold-water bath. Then the solid residues, if any in the reactor, were removed, immersed in acetone for 24 h, washed with distilled

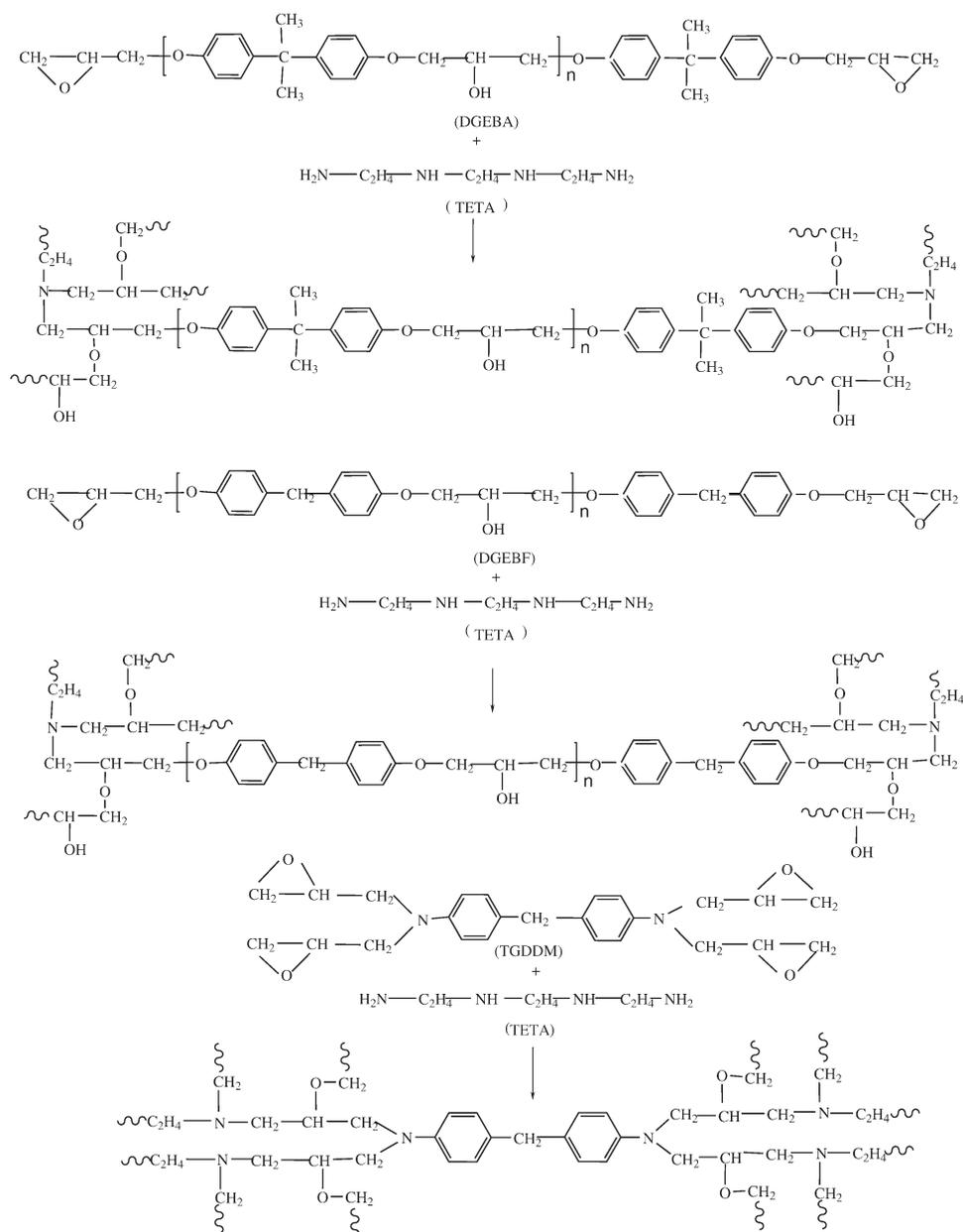


Figure 1. Chemical equation of epoxy resins and curing agent.

water, and dried in a vacuum oven. Finally, the solid products obtained were weighed to calculate the decomposition rate using the following formula (2). The decomposition ratio was averaged with each experiment repeated two times.

$$R_d = \frac{(m_o - m_d)}{m_o} \times 100\%, \quad (2)$$

where R_d represents the decomposition ratio, m_o represents the mass of original resin, m_d represents the mass of the dried solid residue after near-critical water treatment. The corresponding acetone was collected to identify the liquid products by gas chromatography-mass spectrometer (GC-MS). The liquid phase products were analyzed by GC-MS which was made by Agilent. The spectra were recorded with a 6890NGC-5973NMS,

equipped with a chromatographic column of DB-5MS (30 m × 0.25 mm × 0.25 μm).

It was observed that a yellowish brown decomposed compound with high viscosity, namely “liquid phase” appeared in the upper and bottom of solution. The remaining undissolved specimen cleaned with acetone is termed “solid phase.”

RESULTS AND DISCUSSION

Decomposition Process of Epoxy Resin

Decomposition temperature is an important operating parameter for the recycling process. As expected, the decomposition of DGEBA/TETA epoxy matrix was facilitated at higher temperature. The decomposition reactions were conducted at

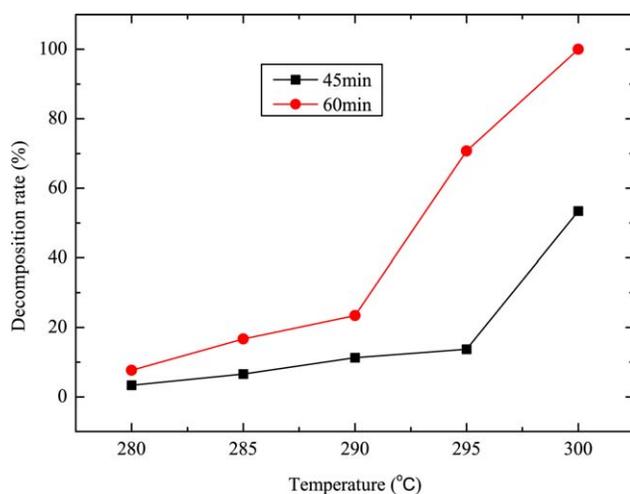


Figure 2. Decomposition rate of DGEBA/TETA system versus temperature in different reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperatures ranging from 280 to 300°C for 45 and 60 min, respectively, with a feedstock of 1 g epoxy resin: 10 mL water. Figure 2 displays the percentage of decomposition as a function of reaction temperature, being 3.3, 11.2, 53.4% at 280, 290, and 300°C for 45 min, and being 7.7, 23.4, 100% at 280, 290, and 300°C for 60 min, respectively. The cured solid epoxy resin was observed to become tougher with more cracks with increasing both the reaction temperature and the reaction time. The liquid phase gradually changed from yellowish to nigger-brown.

The decomposition rate of the DGEBA/TETA system was studied at 280, 285, 290, 295, 300, and 305°C, with a feedstock ratio of 1 g resin: 10 mL water for 45 and 60 min. Figure 3 presents the decomposition rate as a function of reaction temperature and reaction time. With increasing the decomposition rate, the solid residues turned from transparency to translucency and the cracks were observed on the residue surface while water and acetone were still clear and colorless. When the temperature was below 290°C, the processes obey 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, the decomposition process was very lengthy, the decomposition rate was less than or close to 10%. Although the temperature was between 290 and 295°C, degradation reaction was rapid decomposition process. The three-dimensional network structure of epoxy resin system was destroyed, so decomposition rate increased rapidly, the percentage of decomposition was increased to 68.2%. The shape of the solid residues was observed to be changed. The surface became damaged with more cracks. Accordingly, water became opaque and the acetone solvent turned yellowish. These phenomena combined with a higher percentage of decomposition indicate the occurred internal decomposition, and the partially destroyed cross-linked structure during this process. When the temperature was above 295°C, it was to continue to slow decomposition process. The decomposition reached 100% at 305°C for 60 min. However, the corresponding acetone solvent was dark-brown.

The decomposition rate of the TGDDM/TETA system was studied at 300, 310, 320, 330, 340, and 350°C, with a feedstock ratio

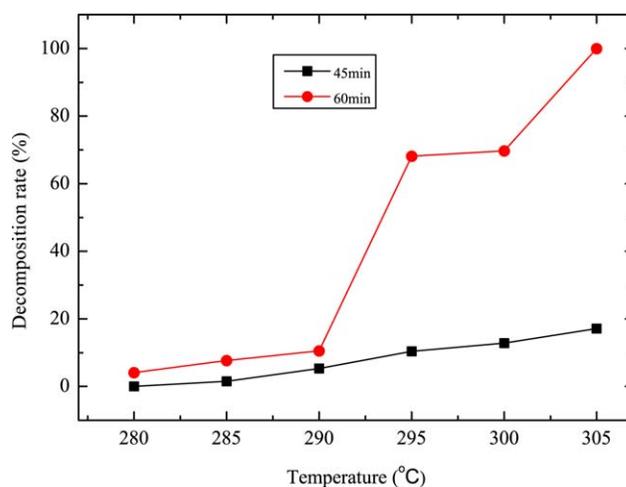


Figure 3. Decomposition rate of DGEBA/TETA system versus temperature in different reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 1 g resin: 10 mL water for 45 min and 60 min. Figure 4 presents the decomposition rate as a function of reaction temperature and reaction time. With increasing the decomposition rate, the solid residues turned from transparency to translucency and the cracks were observed on the residue surface while water and acetone were still clear and colorless. The decomposition rate was calculated to be less than 10%, when the temperature was below 310°C. Although the temperature reached 310°C, the decomposition rate was 8.2% (45 min) and 16.9% (60 min), respectively. The surface of sample became damaged with more cracks and the samples became black, indicating that the carbonation reaction occurred. Accordingly, water became opaque and acetone turned to black brown. The percentage of decomposition rate reached 100% at 350°C. However, the corresponding acetone changed from black brown to black. These indicate that the network structure of epoxy resin had become loose and porous and the solvent had destroyed the resin system. The results showed that high temperature favored the decomposition

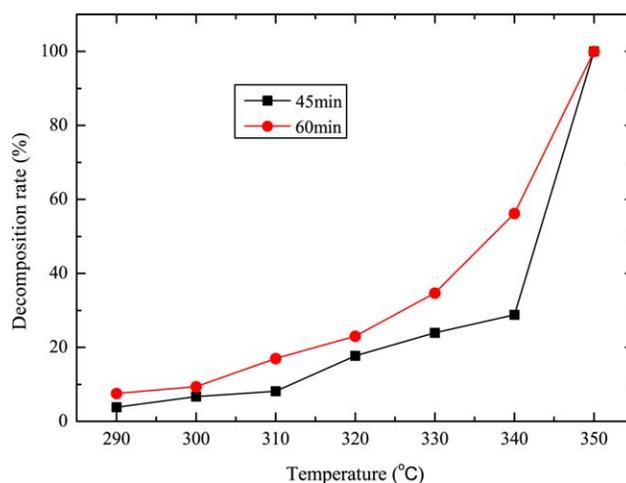


Figure 4. Decomposition rate of TGDDM/TETA system versus temperature in different reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Main Components of DGEBA/TETA System (290°C; 60 min)

Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	14.5608	Bisphenol A		228	59.0565

of epoxy resins owing to two effects. The first is the decreased water viscosity that could increase the reacting substance diffusion and improve the decomposition rate of resins. The second is the dissociation of water that can give more H^+ and OH^- to participate in the reaction. To know the identity of fragments produced in the degradation, the liquid phase evolved was collected and studied by gas chromatography coupled with mass spectrometry.

GC/MS Analysis of Liquid Phase Decomposition Products

The utility of the technique is based on the application of thermal energy to produce volatile fragments and products from macromolecule-compounds capable of being analyzed using GC/MS. The production of these analytes is reproducible and follows chemical principles, which permit the interpretation of results applied to unknown polymers. The presence and absence of specific peaks in the program not only differentiate one sample from another, but also may be crucial in identifying the defects related to product performance. The liquid phase of decomposition products was analyzed by GC/MS.

Product Analysis of DGEBA/TETA System. Tables I–III show the products of DGEBA/TETA system at different temperatures after 60 min. Several products could be identified, which gave some information about the degradative processes. The cleavage of a bond in the resin yields two radicals, which are saturated by hydrogen abstraction from a donor molecule.²¹ The bonds that are the most likely to break were examined in GC-MS experiments. The first reaction to occur when heating epoxy resins is the elimination of water from the secondary alcohol group (i). The resulting allylic bonds easily undergo hemolysis and the free radicals are saturated by hydrogen abstraction (ii).

In the first fraction, obtained after 60 min at 290°C, bisphenol A was identified from the GC spectra, Supporting Information Figure S4, and formed by the breakage of ether linkages of the

units introduced by DGEBA. There should be other substances, but they may not be detected by gas chromatography-mass spectrometry. For example, the decomposition products of large molecular weight could not be gasification and enter the chromatographic column, so they were not shown in the test results. Thus, at 295°C not only ether groups are broken but also C–C linkages from the GC spectra, Supporting Information Figure S5. At 300°C, bisphenol A, phenol, *p*-isopropyl phenol, *m*-isopropylphenol, and *p*-isopropenylphenol were identified from the GC spectra, Supporting Information Figure S6, meaning that ether groups are broken much easier than carbon–carbon linkages. It was found that the main chain of bisphenol A was easily broken,²² because bisphenol A type possessed quaternary carbon atom, which was susceptible to be attacked by acid to produce tertiary positive ions. Because the stability of the tertiary carbenium ion is the best, the degradation process would shift in the direction of the decreased energy, which is depicted in Scheme 1.

Product Analysis of DGEBA/TETA System. Tables IV and V show the products of DGEBA/TETA system at different temperatures after 60 min. Several products (bisphenol compounds) could be identified from the GC spectra, Supporting Information Figures S7 and S8. The first step and the second step reaction process were the same. The direct product of 4,4'-methylenebis-phenol underwent a series of complicated rearrangement to form final products (iii). However, bisphenol F type epoxy resin (BPF) possessed methylene group ($-CH_2-$) in the center of main chain, which was not susceptible to be attacked by acid to produce tertiary positive ions, so the degradation products were completely different from bisphenol A (BPA). The mechanism is shown in Scheme 2.

Product Analysis of TGDDM/TETA System. In general, the degradation mechanisms experienced by polymers are free-

Table II. The Main Components of DGEBA/TETA System (295°C; 60 min)

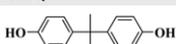
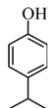
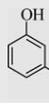
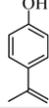
Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	7.65184	Phenol		94	17.3508
2	9.7445	<i>m</i> -Isopropylphenol		136	3.9294
3	14.5043	<i>p</i> -Isopropenylphenol		134	15.7859
4	14.656	Bisphenol A		228	38.0562

Table III. The Main Components of DGEBA/TETA System (300°C; 60 min)

Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	7.4775	Phenol		94	15.6408
2	9.1768	<i>p</i> -Isopropylphenol		136	8.4893
3	9.2293	<i>m</i> -Isopropylphenol		136	7.5169
4	14.656	<i>p</i> -Isopropenylphenol		134	15.0815
5	14.5589	Bisphenol A		228	16.5411

radical processes initiated by the bond dissociation at high temperatures. The specific pathway followed by a particular polymer is related to the relative strength of polymer bonds and the structure of the polymer chain. These mechanisms are grouped into three categories: random scission, unzipping, and side-group elimination.²³

From Tables VI–VIII, the composition of the decomposed compounds was complex and the main components were a mixture

of anilines, quinolines, and indoles from the GC spectra, Supporting Information Figure S9. The content of quinolines and indoles increased with increasing the temperature from the GC spectra, Supporting Information Figure S10, while the content of anilines decreased with increasing the temperature from the GC spectra, Supporting Information Figure S11. It may be seen that high temperature (pyrolysis) has the potential to enable a “closed-loop” recycling scheme for TGDDM/TETA resin system.

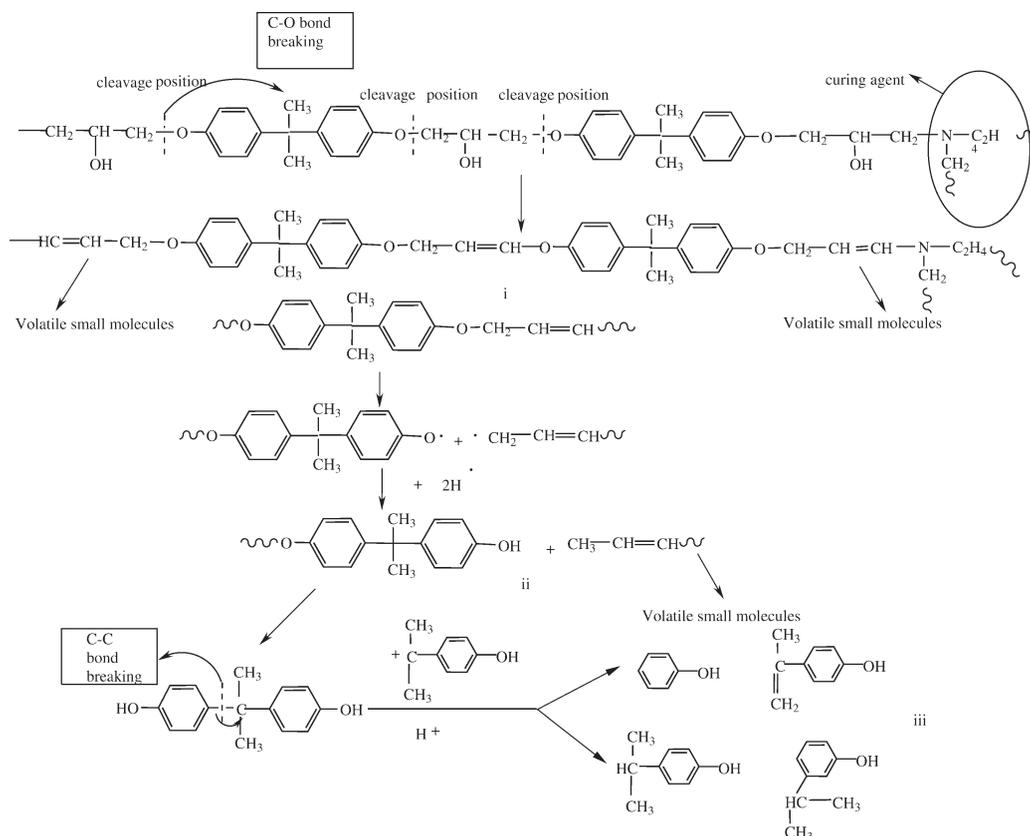
**Scheme 1.** Possible decomposition mechanism of the DGEBA/TETA system in near-critical water.

Table IV. The Main Components of DGEBF/TETA System (300°C; 60 min)

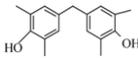
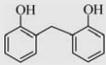
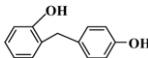
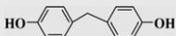
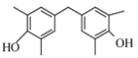
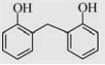
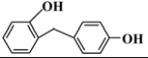
Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	3.535	Toluene		92	10.98
2	12.347	4,4'-Methylenebis[2,6-dimethyl-Phenol]		256	7.701
3	13.508	2,2'-Methylene bis-Phenol		200	24.860
4	13.682	2-[[4-Hydroxyphenyl)methyl]-Phenol		200	43.390
5	14.198	4,4'-Methylenebis-Phenol		200	3.642

Table V. The Main Components of DGEBF/TETA System (305°C; 60 min)

Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	3.351	Toluene		92	39.682
2	12.361	4,4'-Methylenebis[2,6-dimethyl-Phenol]		256	4.662
3	13.598	2,2'-Methylenebis-Phenol		200	10.765
4	13.776	2-[[4-Hydroxyphenyl)methyl]-Phenol		200	11.663

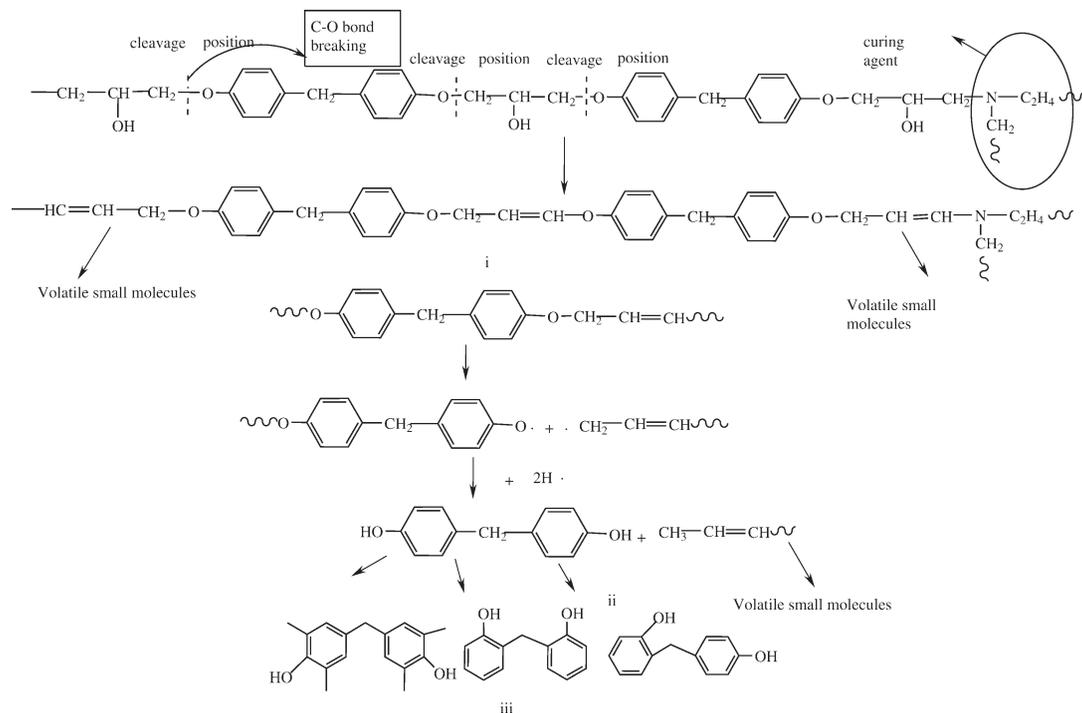
**Scheme 2.** Possible decomposition mechanism of the DGEBF/TETA system in near-critical water.

Table VI. The Main Components of TGDDM/TETA System (330°C; 60 min)

Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	4.084	3-Penten-2-one,4-methyl-		98	1.101
2	6.560	Aniline		93	25.2475
3	7.569	Aniline, N-methyl-		107	7.0945
4	7.687	o-Toluidine		107	6.6097
5	7.833	Benzenamine, N,N-dimethyl-		121	7.7254
6	8.457	Benzenamine, N-ethyl-		121	4.5904
7	9.233	Benzenamine, N,N,4-trimethyl-		135	0.8776
8	9.978	N-Ethyl-p-toluidine		135	1.8683
9	10.545	Benzeneacetonitrile, .alpha.-methylene-		129	0.6477
10	11.6792	1H-Indole, 2,3-dihydro-1-methyl-		133	1.6303
11	11.8834	6-Methyl-1,2,3,4-tetrahydroquinoline		147	2.3367
12	12.7428	1H-Indole, 2-methyl-		131	0.2093
13	14.438	2,3,7-Trimethylindole		159	0.347
14	15.3541	Julolidine		173	0.6263

In this case, the resins were simply unzipped at high temperatures, generating mostly monomers. Instead of a series of increasingly longer oligomers, the tables show large monomers, such as anilines, quinolines, and indoles. In the epoxy resin polymer, the weakest bonds are those holding the chains together, so high temperature degradation produces either fragmentation to smaller oligomeric units or unzipping all the way to monomers. However, the groups attached to the side of the chain are held by bonds, which are being the ether bond, supplemented by carbon and nitrogen bond. The degradation mechanisms experienced by epoxy resin polymers are free-radical processes initiated by bond dissociations at high temperature, so ether groups were eliminated. Simultaneously, short carbon chain was unzipped to produce quinolines and indoles. The decomposition mechanism was shown in Scheme 3.

The Calculation of Crosslinking Degree of Three Resins Systems. For dynamic mechanical analysis, the prepared resin systems meet the following two conditions:

1. The system is at a stable high elastic state at high temperature.
2. The strain is very small, only around 1%.

Thus, the system is considered to be in accordance with Hooke's law in this range. According to the aforementioned two points, the crosslinking degree of the resin system can be tested by rubber theory.²⁴

$$E \approx \frac{3\rho RT}{\bar{M}c}, \quad (3)$$

where E is the storage modulus at $T_g+50^\circ\text{C}$ (MPa), ρ is the polymer density (g/cm^3), R is gas constant ($\text{J}/\text{mol K}$), T is absolute temperature (K), $\bar{M}c$ is the average relative molecular mass between junction network.

$$\frac{E}{3RT} = \frac{\rho}{\bar{M}c} = \frac{m}{V \times \bar{M}c} = \frac{\bar{M}c \times N}{V \times \bar{M}c} = \frac{N}{V}, \quad (4)$$

where V is unit volume (g/cm^3), M is the quality of the unit volume of polymer (g), N is the number of network chain on crosslinking network, the degree of crosslinking.

Table VII. The Main Components of TGDDM/TETA System (340°C; 60 min)

Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	4.168	3-Hexen-2-one		98	0.98653
2	6.556	Aniline		93	12.4196
3	7.596	Aniline, N-methyl-		107	3.8559
4	7.714	p-Aminotoluene		107	3.7590
5	7.839	Benzenamine, N,N-dimethyl-		121	5.4784
6	8.506	Benzenamine, N-ethyl-		121	2.8252
7	10.452	Quinoline		129	1.2366
8	10.769	1H-Indole, 7-methyl-		131	0.8593
9	11.428	Indolizine		117	1.0257
10	11.646	1H-Indole, 2,3-dihydro-1-methyl-		133	2.1725
11	12.165	Quinoline, 6-methyl-		143	1.2193
12	12.873	1H-Indole, 2-methyl-		143	0.4409
13	13.896	Indolizine, 2,5-dimethyl-		145	1.7200
14	14.003	1H-Indole, 2,3-dimethyl-		145	0.6676
15	14.407	1H-Indole, 1,2,3-trimethyl-		159	0.5334
16	15.331	Julolidine		173	1.8709

The data of Table IX displayed the degree of crosslinking of DGEBA/TETA, DGEBF/TETA, TGDDM/TETA, which were 2.4×10^{-3} , 2.9×10^{-3} , and 4.0×10^{-3} mol/cm³, respectively. In fact, the bigger the crosslinking degree, the more per unit volume of crossline bond, the better heat resistant performance of the resin. So the decomposition temperature of TGDDM/TETA system is higher than the decomposition temperature of the other two systems when they obtained the same decomposition rate. Simultaneously, because the degree of crosslinking of DGEBA/TETA and DGEBF/TETA systems was similar, there was little difference between the two systems of the decomposition parameter.

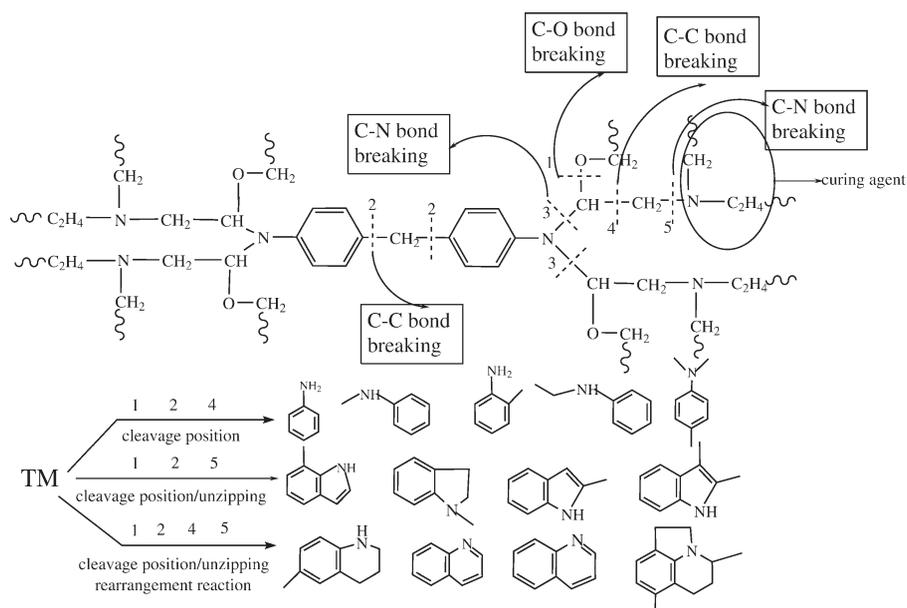
CONCLUSION

Significant differences were observed among different epoxy systems, which could be attributed to different chemical structures, reaction condition such as DGEBA and DGEBF, and

molecule structures of the main chain, although their degradation temperature and the degradation pressure are similar. For glycidyl ether resins, the ether bonds of main chain were the most vulnerable, bisphenol F type epoxy resin(BPF) possessed methylene group($-\text{CH}_2-$) in the center of main chain, however, bisphenol A type possessed quaternary carbon atom, which was susceptible to be attacked by acid to produce tertiary positive ion, their degradation mechanisms are different. The near-critical water degradation of polymers has demonstrated two distinct simultaneously occurred reactions in the reactor. One is a random scission of links which causes a molecular weight reduction of the raw polymer, and the other is a chain-end scission of C—C bonds, which causes the generation of the volatile product. The chain-end scission takes a place at the gas–liquid interface in the working reactor. The experimental results indicate that high temperature water degradation mechanism involved unzipping, and side group

Table VIII. The Main Components of TGDDM/TETA System (350°C; 60 min)

Number	Retention time (min)	Components	Structure	Mol wt	Relative area %
1	4.0456	3-Hexen-2-one		98	0.75884
2	6.579	Aniline		93	12.1797
3	7.421	Aniline, N-methyl-		107	4.6770
4	7.512	p-Aminotoluene		107	7.5063
5	7.9712	Benzenamine, N-ethyl-		121	3.5656
6	8.3854	Benzenamine, N,N,4-trimethyl-		135	0.6823
7	9.008	Quinoline		129	1.9681
8	9.283	1H-Isoindole, 3-methoxy-1-methyl-		161	2.722
9	9.709	6-Methyl-1,2,3,4-tetrahydroquinoline		147	1.441
10	10.020	1H-Indole, 3-methyl-		131	3.2513
11	10.693	1H-Indole, 2,3-dimethyl-		145	5.53302
12	11.095	1H-Indole, 5,6,7-trimethyl-		159	1.3387
13	11.292	1H-Indole, 2,3,5-trimethyl-		159	1.6073
14	11.518	1,2,3,7-Tetramethylindole		173	0.4603
15	11.634	4H-Pyrrolo[3,2,1-ij] 1,2,5,6-tetrahydro-4-methyl-quinoline		173	0.3214



Scheme 3. Possible decomposition mechanism of the TGDDM/TETA system in near-critical water.

Table IX. The Crosslinking Degree of Three Resins System

Epoxy resin	DGEBA	DGEBF	TGDDM
T_g (°C)	115.9	93.0	223.0
Storage modulus (MPa) ($T_g+50^\circ\text{C}$)	6.95	6.79	22.7
The degree of crosslinking (mol/cm^3)	2.4×10^{-3}	2.9×10^{-3}	4.0×10^{-3}

elimination, the resins tended to form longer oligomers at lower temperatures with the random scission.

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