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Chemical degradation of TGDDM/DDS epoxy resin in supercritical 1-propanol: Promotion effect of hydrogenation on thermolysis

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ABSTRACT

Chemical decomposition of an epoxy system made of tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) and 4,4′-diaminodiphenylsulfone (DDS) in supercritical 1-propanol was investigated under different reaction temperature and time. The GC–MS results suggested that the epoxy system was decomposed to the products including aniline, N-propylbenzenamine, and 4,4′-diaminodiphenylsulfone. The change of the products' yield with time was measured by GC. In addition, the formed chars were characterized by SEM, elemental analysis, Raman and XRD. The results implied the presence of some graphite microcrystals and disordered structure in the solid residue. Upon the addition of KOH, the Guerbet reaction of 1-propanol was promoted to generate more hydrogen. A possible free-radical reaction mechanism was proposed for the depolymerization of TGDDM/DDS epoxy resin. Hydrogenation of radicals had a promotion effect on thermolysis of TGDDM/DDS epoxy resin.

1. Introduction

Tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) cured with 4,4′-diaminodiphenylsulfone (DDS) possesses a high glass-transition temperature (T_g) and a high density cross-linked network, and is extensively used as a binder for high-performance and light-weight composites in the aviation industry [1,2]. However, the disposing of the epoxy resin becomes an urgent issue when these products reach the ends of their service lives. Both landfill and incineration disposal are not optimal, for environmental regulations may eventually implement a ban on them [3]. Epoxy resins are insoluble and infusible in any solvents because of the cross-linked network structure, and remain as barriers for efficient recycling. The recycling technologies for the decomposition of epoxy resins mainly involve pyrolysis [4–10] and solvolysis [11–16]. The pyrolysis of epoxy resin is usually performed at high temperature, and inevitably generates greenhouse gases (CH_4 and CO_2), toxic substances (CO, benzene and toluene) and low-value by-products (char and tar). The solvolysis processes either use harsh reagents such as nitric acid or are not convenient to reach the conditions such as subcritical water. Therefore, the recycling technologies for epoxy resin should be improved to reclaim useful degradation products in a sustainable manner that is inherently non-toxic to live things and the environment.

Hydrogenolysis of epoxy resin offers a new attractive alternative route for chemical decomposition of epoxy resin. Braun et al. [17] used hydrogen donors such as tetralin and 9,10-dihydroanthracene to cleave various thermosets including anhydride-cured epoxy resin, phenolic resins, melamine resins and unsaturated polyester. Sato et al. [18] used tetralin, decalin, and cyclohexanol to reclaim amine-cured epoxy resin at 440 °C and 2.5 MPa. After 1 h of reaction, a conversion of 98% was achieved due to the hydrogen-donating properties of these solvents. Supercritical alcohol represents an alternative for the use of supercritical water not only since the critical conditions are less extreme [19–22] but also since the hydrogen are in situ produced from the alcohol solvent [23,24]. Jiang et al. [22] monitored the decomposition process of epoxy resin in supercritical isopropanol using the change of the refractive index (RI) of the exit solution with time, identified the Guerbet reaction of alcohol solvents, and concluded that thermolysis played an important role in cleaving the chemical bonds of the epoxy resin. However, the decomposition process of epoxy resin and analysis of the degradation products deserved further investigation.

The objective of this paper is to decompose TGDDM/DDS epoxy resin using supercritical 1-propanol. The main products in decomposition liquids were identified by GC–MS, and the decomposition process of TGDDM/DDS epoxy resin was monitored

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by the change of the products' yield with time. Furthermore, the formed chars were characterized by SEM, elemental analysis, Raman and XRD, and the gaseous mixture products were measured by GC. A possible mechanism for the decomposition of the resin in supercritical 1-propanol was discussed.

2. Experimental

2.1. Materials

TGDDM and DDS were purchased from Shanghai Research Institute of synthetic resins and Sinopharm Chemical Reagent Co., Ltd, respectively. The epoxy resin bar was prepared by dissolving DDS in TGDDM with a stoichiometric equivalent ratio at 120 °C until a homogeneous solution was obtained. The above blend was poured into a polytetrafluoroethane (PTFE) mold (50 mm × 10 mm × 2 mm), and heated at 130 °C for 1 h before they were cured at 180 °C for 4 h. The chemical structures of epoxy resin, curing agent and cured resin are shown in Fig. 1. The reaction medium, 1-propanol, was obtained from Tianjin Dengfeng Chemical Reagent Corporation (China). The standard samples of aniline, N-propylbenzenamine, diphenyl methane, all of them of 99.0 wt% purity, were purchased from the Aladdin Industrial Corporation.

2.2. Degradation of epoxy resin

The degradation of TGDDM/DDS bar was conducted in a stainless steel autoclave with a volume of 0.5 L. The internal temperature of the autoclave was monitored by connecting to a PID controller, and the pressure was detected by a pressure gauge with a safety valve. A stainless steel pipe with a needle valve was connected with the autoclave, and used as a sampling device. A water cooling system was fixed around a section of the pipe which located between the autoclave and the needle valve.

Epoxy resin bars and 0.2 L of 1-propanol with or without potassium hydroxide (1 wt%) were charged into the autoclave. The internal temperature of the autoclave was raised and held at one of a range of temperature from 280 to 340 °C with a regular interval of 10 °C. The degradation time of the epoxy resin in supercritical 1-propanol varied from 1 h to 5 h. After the needle valve was cautiously switched on, the sample extraction was performed by collecting 1.5 mL of degradation solution in a sample bottle. Then, the needle valve was switched off, and the degradation reaction proceeded. After a regular period of time, the sample extraction was repeated. When the degradation reaction of TGDDM/DDS was finished, the autoclave was cooled to room temperature. The decomposition liquid was collected for GC–MS analysis. The solid residue was weighted and characterized after washing with fresh 1-propanol and drying in an oven at 110 °C for 24 h. A gas-sampling bag was used for the capture of the gaseous mixture and subsequent injection of the gas sample into gas chromatography.

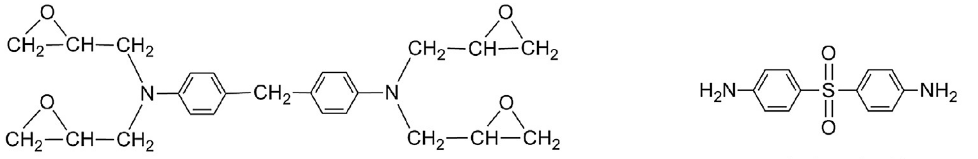
2.3. Characterization

Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Nicolet Magna- IR 750 spectrometer using the usual KBr pellet method. The cross-linking degree of the cured epoxy resin was determined by comparing the heat with a DSC 200 F3 Maia (Netzsch, Germany) (Equation (1)). Samples were heated from 40 °C to 300 °C at the heat speed of 5 °C min^{-1} under nitrogen atmosphere.

$$\text{Cross} - \text{linking degree} = (\Delta H_{\text{uncured}} - \Delta H_{\text{cured}})/\Delta H_{\text{uncured}} \times 100\% \quad (1)$$

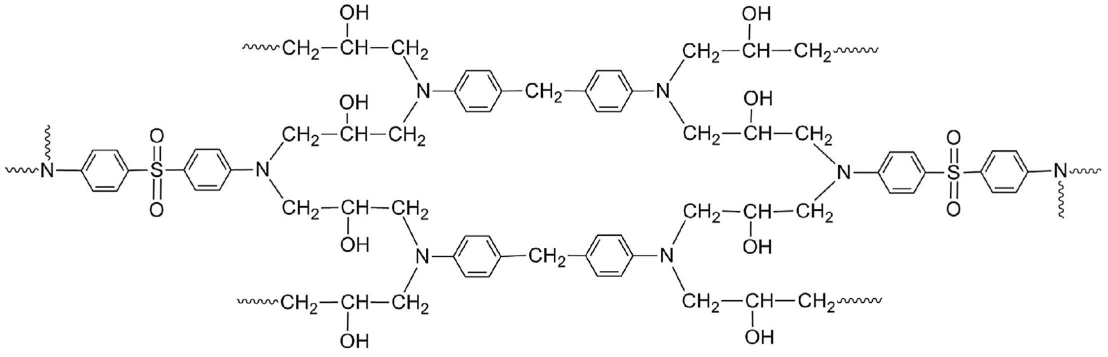
$\Delta H_{\text{uncured}}$: Heat of the uncured resin
ΔH_{cured}: Heat of the cured resin

The gaseous products were measured by two gas chromatographies (GC): Model SP-2305 (Beijing Beifenruili Analytic Instrument (Group) Co.) with pure argon as carrier gas, a 5A molecular sieve column and a TCD detector; Model GC-1790 (Agilent Technologies Shanghai Analytical Instrument Co. LTD), with pure nitrogen as carrier gas, a C_{18} column and an FID detector. The content



Tetraglycidyl 4,4'-diaminodiphenylmethane, TGDDM

4,4'-Diaminodiphenylsulfone, DDS



TGDDM epoxy resin cured with DDS

Fig. 1. Chemical structures of epoxy resin, curing agent and cured resin.

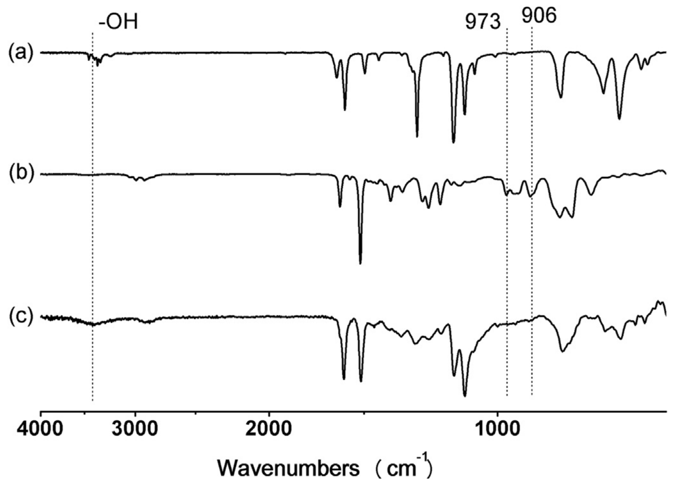


Fig. 2. FTIR spectra of: (a) curing agent (4,4′-diaminodiphenylsulfone, DDS); (b) uncured epoxy resin (tetraglycidyl 4,4′-diamino diphenyl methane, TGDDM); (c) TGDDM resin cured with DDS.

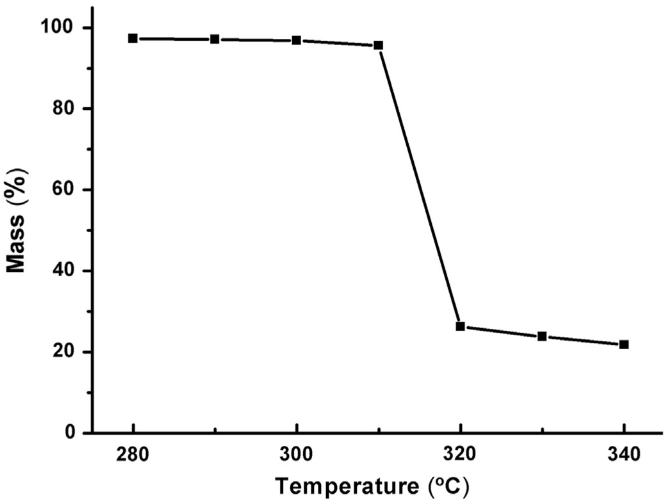


Fig. 3. Temperature-dependent mass profile of TGDDM/DDS resin in supercritical 1-propanol for 1 h.

of CO_2 was determined using an alkali adsorption method. The contents of SO_2 and H_2S were evaluated by a GC with a JD 301 column and a TCD detector.

The degradation solution was analyzed by an Agilent Model 7890 gas chromatograph that was coupled with an Agilent Model 5975 quadrupole mass spectrometer. The analytical column was a HP-5MS 5% phenyl methyl silox capillary column (30 m × 0.25 mm inner diameter (ID), 0.25 μm film thickness). The gas chromatograph was operated in a temperature-programming mode. The column temperature started at 50 °C for 2 min followed by a ramp at 8 °C min^{-1} to 230 °C. The temperature was maintained at 230 °C for 5 min before it was raised to 280 °C at a rate of 10 °C min^{-1}. The temperature was held at the upper temperature for 10 min. The flow rate of the carrier gas (helium) was held at 1.0 mL min^{-1}. All MS analyses were carried out in scan mode (mass range of 40–450 amu) with electron impact ionization (EI) of 70 eV. An autosampler was used to inject samples of 1.0 μL into the gas chromatograph. The identification of the degradation products was based on library data.

A Shimadzu GC-2010 with an FID detector was used to quantitatively analyze degradation liquids. The carrier gas was nitrogen at a flow rate of 1.21 mL min^{-1}. The column was a Restek Rtx-1 type capillary column (30 m × 0.25 mm inner diameter (ID), 0.25 μm film thickness). The injector and the detector temperature were set to 270 °C and the injector split ratio was 1:30. The column temperature started at 50 °C followed by a ramp at 8 °C min^{-1} to 250 °C.

Scanning electron image (SEM) was taken using a LEO 1530VP microscope with an accelerating voltage of 6 KeV. TG-MS experiments (a heating rate of 5 °C min^{-1} under flow of nitrogen gas) were performed using a STA409PC/MS instrument. Elemental analysis was carried out using a Vario EL CUBE elemental analyzer. Raman microprobe examination was performed with a LabRAM HR UV-NIR Raman microspectrometer at an excitation wavelength of 488 nm. X-ray diffraction (XRD) was recorded on a Bruker D8 Advance powder diffractometer.

3. Results and discussion

By means of the calculation in equation (1), the level of crosslinking in the cured epoxy resin was found to be 98.2% complete. In addition, disappearance of the epoxide functions (973, 906 cm^{-1}) and appearance of the hydroxyl functions (3408 cm^{-1}) in FTIR

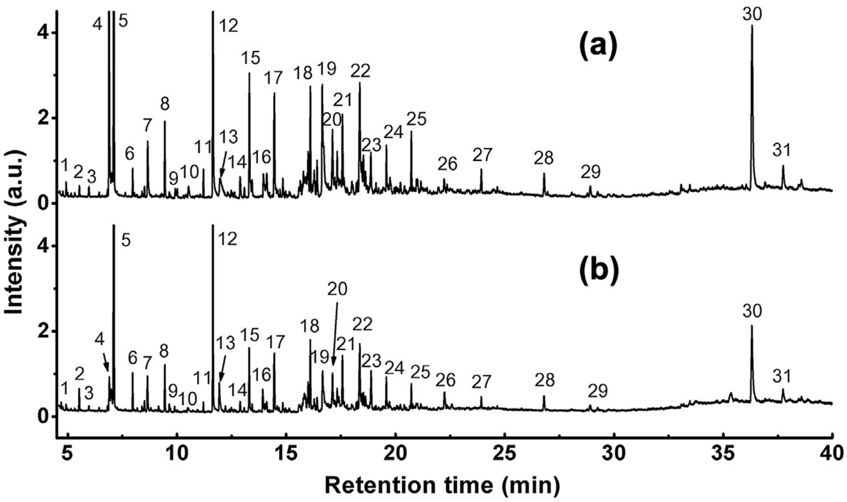


Fig. 4. Total ion chromatograms of the degradation products of TGDDM/DDS resin in supercritical 1-propanol. The degradation was conducted in the batch reactor for 60 min at (a) 340 °C; (b) 320 °C.

Table 1
Main degradation products of TGDDM/DDS in supercritical 1-propanol at 320 and 340 °C.

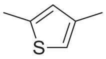
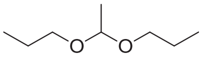
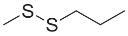
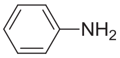
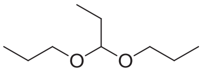
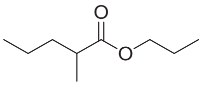
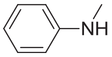
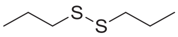
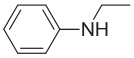
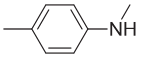
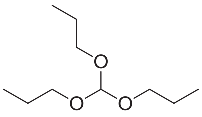
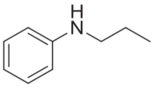
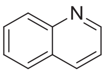
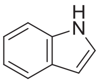
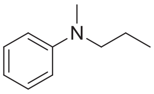
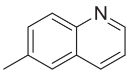
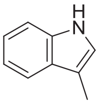
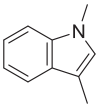
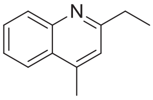
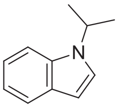
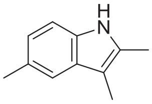
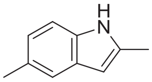
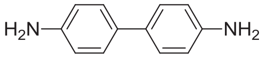
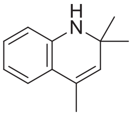
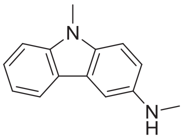
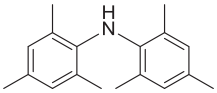
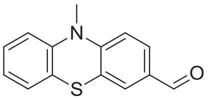
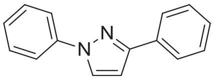
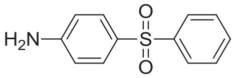
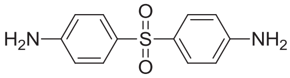
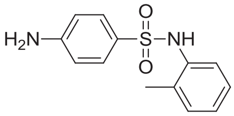
Peak label	Ret. time (min)	Compounds	Molecular structure	Molar mass (g mol^{-1})
1	4.92	2,4-Dimethylthiophene		112
2	5.53	1,1′-[Ethylidenebis(oxy)]-bispropane		146
3	5.97	Methyl propyl disulfide		122
4	6.89	Aniline		93
5	7.11	1,1-Dipropoxypropane		160
6	7.97	Propyl 2-methylvalerate		158
7	8.66	N-methylaniline		107
8	9.44	Dipropyldisulfide		150
9	9.91	N-ethylbenzenamine		121
10	10.52	N,4-dimethylbenzenamine		121
11	11.20	Tripropyl orthoformate		190
12	11.64	N-propylbenzenamine		135
13	11.97	Quinoline		129
14	12.88	Indole		117
15	13.32	N-methyl- N-n-propyl benzenamine		149
16	13.96	6-Methylquinoline		143
17	14.45	3-Methyl-1H-indole		131
18	16.10	1,3-Dimethyl-1H-indole		145

Table 1 (*continued*)

Peak label	Ret. time (min)	Compounds	Molecular structure	Molar mass (g mol^{-1})
19	16.65	2-Ethyl-4-methylquinoline		171
20	17.12	1-Isopropyl-1H-indole		159
21	17.57	2,3,5-Trimethyl-1H-indole		159
22	18.37	2,5-Dimethyl-1H-indole		145
23	18.87	Benzidine		184
24	19.59	1,2-Dihydro-2,2,4-trimethyl quinoline		173
25	20.73	3-(N-methylamino)-9-methylcarbazole		210
26	22.22	2,4,6-Trimethyl-N-(2,4,6-trimethylphenyl)benzenamine		253
27	23.94	3-Formyl-10-methylphenothiazine		241
28	26.80	1,3-Diphenyl-1H-pyrazole		220
29	28.91	4-Aminodiphenylsulfone		233
30	36.31	4,4′-Diaminodiphenylsulfone		248
31	37.74	4-Amino-N-(2-methylphenyl)- benzenesulfonamide		262

(Fig. 2) also verified the complete cross-linking [13]. Many other peaks were identical to those from the uncured epoxy resin.

The effect of reaction temperature on chemical depolymerization of the epoxy resin was evaluated under the following conditions: a reaction time of 60 min, a feedstock ratio of 2 g epoxy resin/200 mL 1-propanol, and a range of temperature from 280 to 340 °C. Fig. 3 shows temperature-dependent mass profile of TGDDM/DDS resin in supercritical 1-propanol. The epoxy resin bars

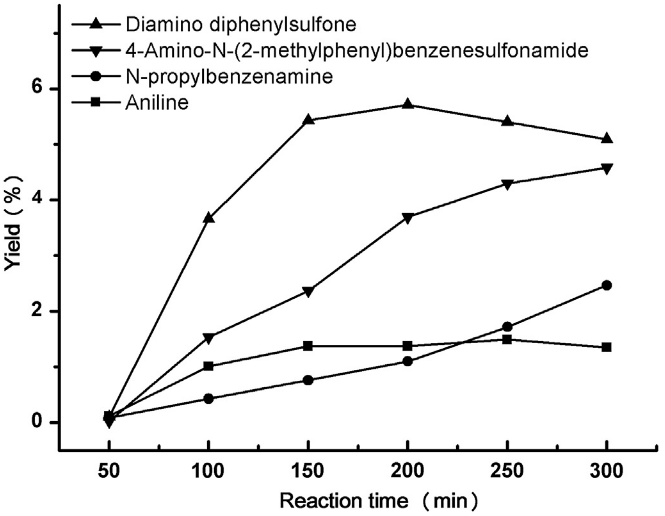


Fig. 5. Yields of the main degradation products versus the reaction time at 320 °C. The yields were determined by GC using diphenyl methane as internal standard.

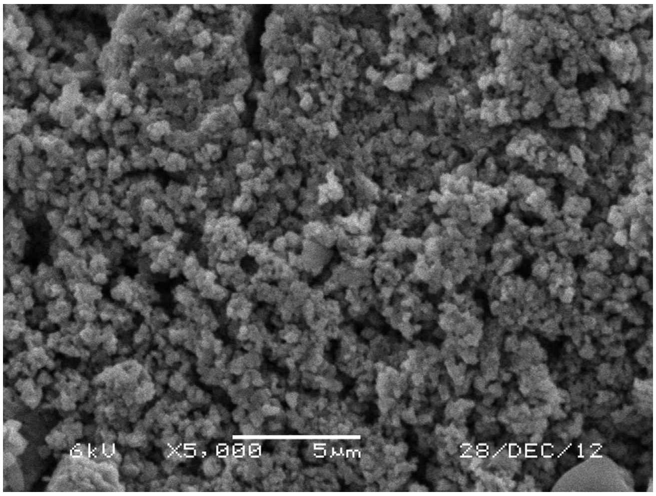


Fig. 6. SEM image of the solid residue after chemical degradation of TGDDM/DDS resin at 320 °C.

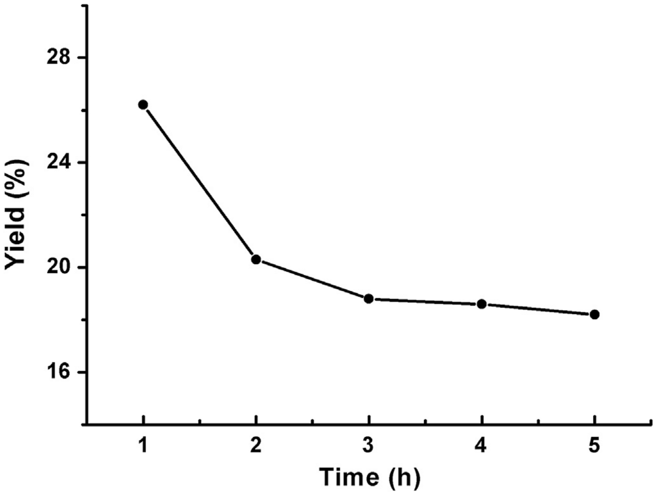


Fig. 7. Yield of the solid residue versus the reaction time at 320 °C.

Table 2
Elemental analysis of the cured epoxy resin and the solid residue obtained in supercritical 1-propanol for different degradation time at 320 °C.

Sample	C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)
TGDDM/DDS[a]	66.75	6.35	14.41	8.18	4.30
TGDDM/DDS[b]	64.58	6.43	17.01	7.92	4.06
SR1	82.90	4.89	4.37	6.95	0.89
SR2	83.30	4.93	3.81	7.05	0.91
SR3	82.07	5.18	4.87	7.04	0.84
SR4	81.64	5.36	5.15	7.10	0.75
SR5	81.79	5.36	5.07	7.04	0.74

SR1 = the solid residue obtained after 1 h, SR2 = the solid residue obtained after 2 h, and so on.

[a] TGDDM/DDS = the theoretical values of the cured epoxy resin.

[b] TGDDM/DDS = the experimental values of the cured epoxy resin.

remained in the original shape, and retained 97.3 to 95.6 wt% of mass in the temperature range 280–310 °C. However, the epoxy resin bars collapsed, and 26.2 to 21.8 wt% of mass remained in the temperature range 320–340 °C. The colors of the degradation liquids darkened from clear, light brown to deep brown with the temperature rise. Therefore, thermolysis played a key role in decomposing the chemical bonds of the epoxy resin, and an initial decomposition temperature was about 320 °C for the epoxy resin used in this study under the conditions mentioned above.

Fig. 4 shows the total ion chromatograph (TIC) of the decomposition products of TGDDM/DDS resin in 1-propanol solution at 320 and 340 °C. As shown in Fig. 4, the decomposition products of the epoxy resin in supercritical 1-propanol at 340 °C were similar to that obtained at 320 °C. The assignment of the main degradation products is summarized in Table 1. The decomposition products contained aniline, N-propylbenzenamine, and their complex

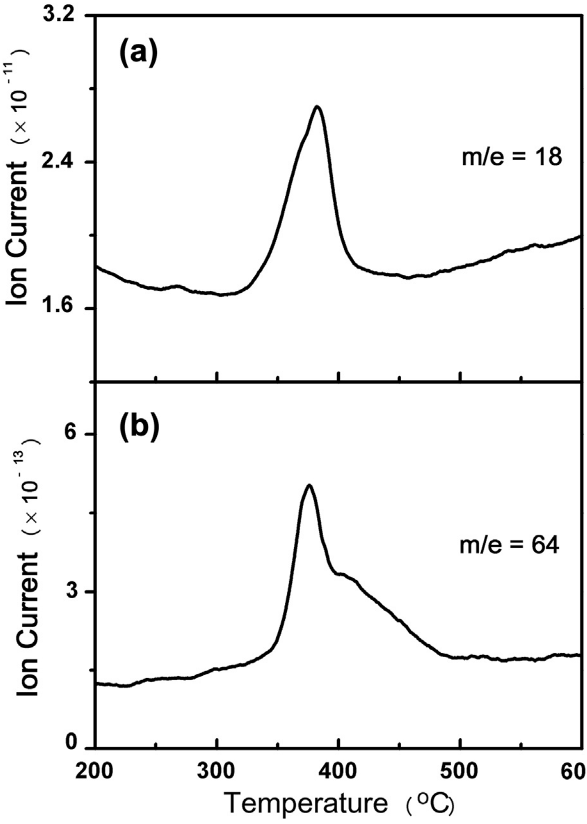


Fig. 8. TG–MS analysis of TGDDM/DDS resin at (a) m/e 18; (b) m/e 64.

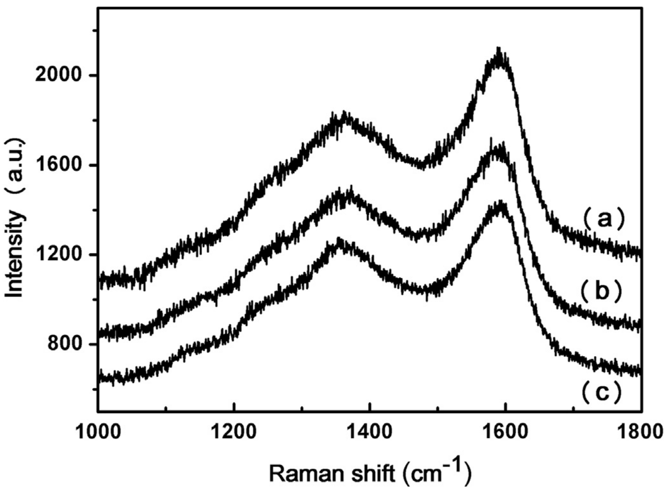


Fig. 9. Raman spectrum of the solid residue acquired at 320 °C in supercritical 1-propanol for different degradation time: (a) 2 h, (b) 3 h, (c) 5 h.

Table 3
Composition of the gas mixture collected from the batch reactor after the degradation of TGDDM/DDS resin in supercritical 1-propanol.

Component	General (%)	Without O_2 and N_2 (%)
H_2	22.57	55.05
O_2	6.19	–
N_2	52.81	–
CH_4	1.37	3.35
CO	2.46	6.00
CO_2	2.88	7.03
C_2H_4	0.09	0.22
C_2H_6	1.34	3.26
C_3H_6	1.18	2.88
C_3H_8	1.22	2.97
H_2S	5.10	12.43
SO_2	2.80	6.80

derivatives. In addition, sulfur containing compounds such as 2,4-dimethylthiophene, methyl propyl disulfide, dipropyldisulfide, and 4,4′-diaminodiphenylsulfone were also present in the 1-propanol solution.

The quantitative analysis of the main decomposition products such as aniline, N-propylbenzenamine, 4,4′-diaminodiphenylsulfone, and 4-amino-N-(2-methylphenyl)benzenesulfonamide was carried out by taking samples regularly from the reactor for gas chromatography. At 320 °C, the yield of 4,4′-diaminodiphenylsulfone was higher than that of aniline and N-propylbenzenamine (Fig. 5). The yield of 4,4′-diaminodiphenylsulfone increased to its maximum of 5.71 wt% after 200 min, and its decomposition became importance when the reaction time was extended from 200 to 300 min. The yields of N-propylbenzenamine and 4-amino-N-(2-methylphenyl)benzenesulfonamide increased gradually during the reaction time of 300 min, and reached the maximum of 2.47 and 4.58 wt%, respectively. Furthermore, the yield of aniline rose to 1.37 wt% after the reaction time of 150 min, and remained the constant amount from 150 to 300 min.

The decomposition of epoxy resin consisted of a series of consecutive reactions. Some degradation products were intermediate products, and others were end products. The yield profiles of the intermediate products were affected by competition between the formation process and the degradation process or the secondary reaction. The typical characteristic of consecutive reaction was that the yield of an intermediate product had a maximum value during the whole process. The yield of an end product monotonously increased. In the decomposition of TGDDM/DDS, 4,4′-diaminodiphenylsulfone and aniline were intermediate products, but 4-amino-N-(2-methylphenyl)benzenesulfonamide and N-propylbenzenamine were end products. 4,4′-Diaminodiphenylsulfone was not only generated from the cured resin, but also degraded to aniline and SO_2. Aniline was not only produced from 4,4′-

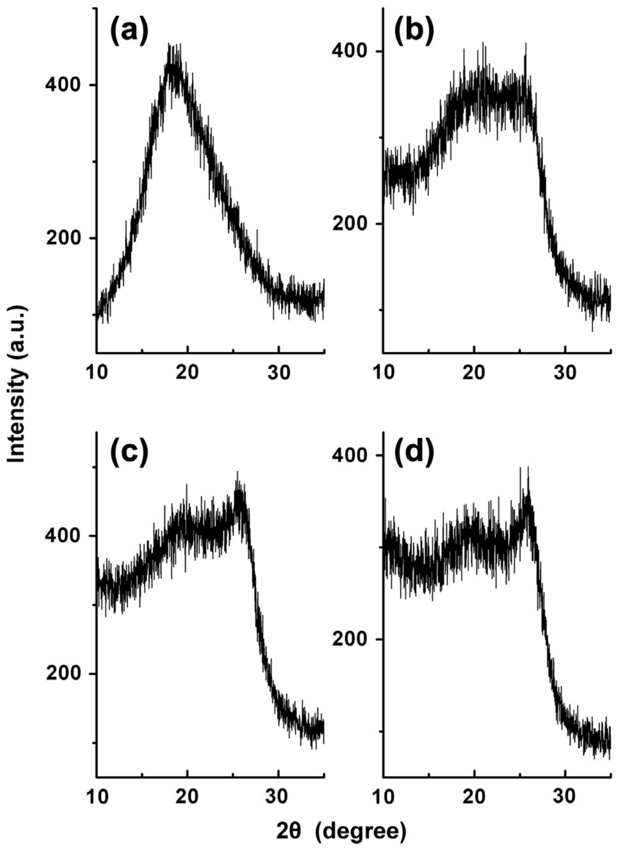


Fig. 10. X-ray diffraction profiles of TGDDM/DDS cured with a molar ratio of 1:1 (a) and after chemical treatment at 320 °C for different degradation time: (b) 2 h, (c) 3 h, (d) 5 h.

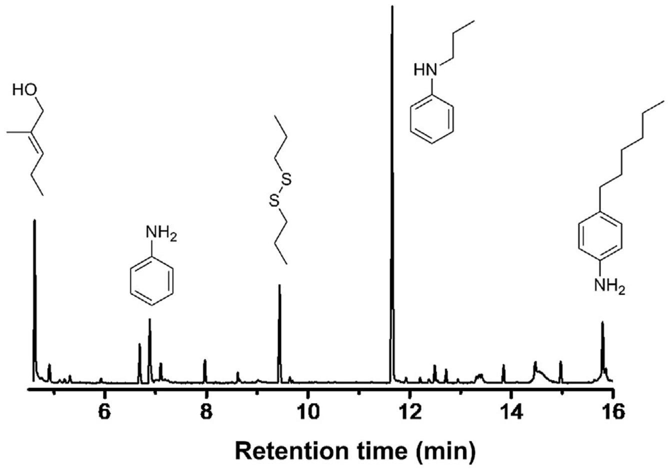
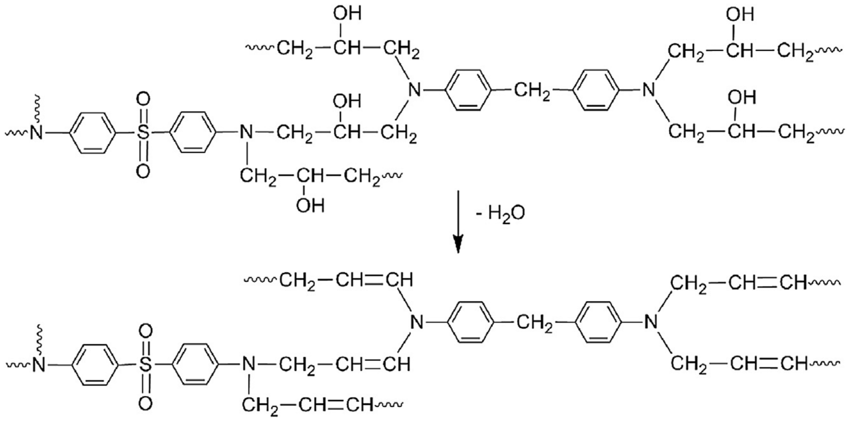


Fig. 11. Total ion chromatogram of the degradation products of 4,4′-diaminodiphenylsulfone in supercritical 1-propanol at 320 °C for 3 h.

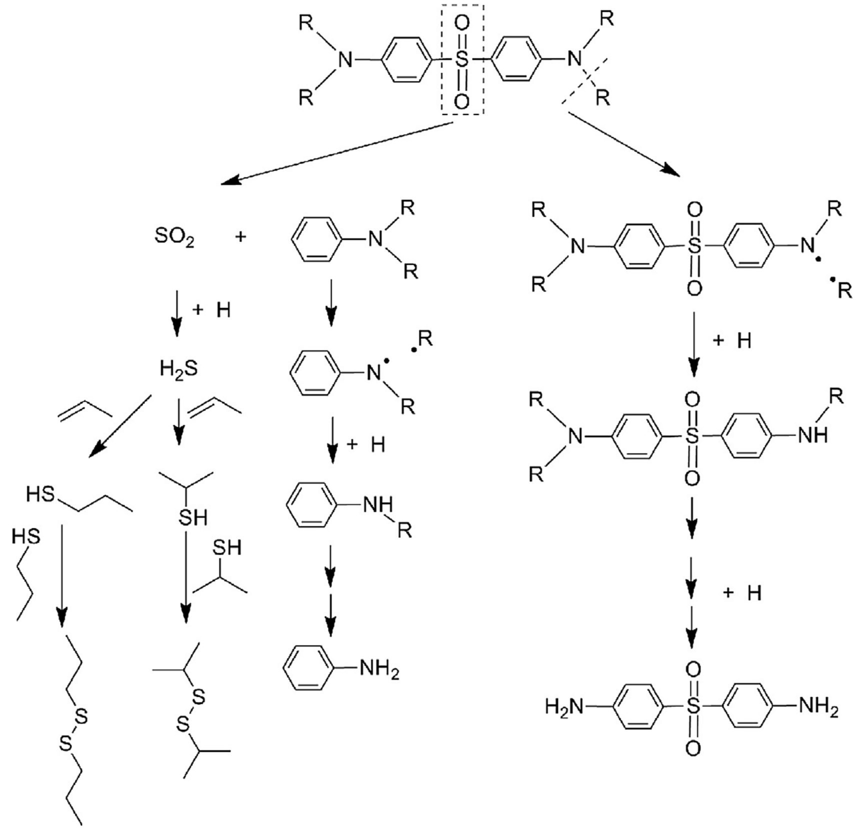


Scheme 1. Elimination of water from the secondary alcohol group of TGDDM cured with DDS.

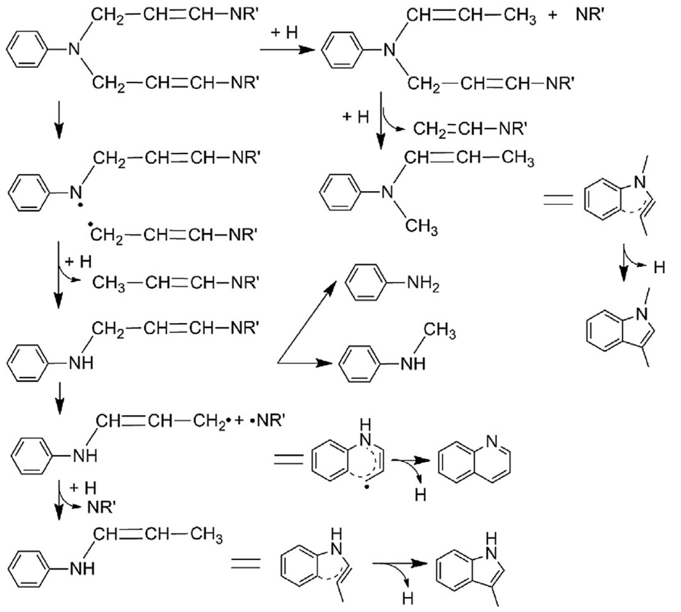
diaminodiphenylsulfone, but also reacted with 1-propanol to form N-propylbenzenamine. Therefore, the yield of 4,4′-diaminodiphenylsulfone or aniline had a maximum value, while the yields of 4-amino-N-(2-methylphenyl)benzenesulfonamide and N-propylbenzenamine monotonously increased.

In addition to organic molecules in 1-propanol solution, some black solid residue formed during the chemical degradation of the epoxy resin. Fig. 6 presents typical morphology of the undesired solid residue. The diameter of the particles was in the micron order. The yield of the solid residue (Fig. 7) reduced to 20 wt% after a reaction time of 2 h, and remained 18 wt% from 3 to 5 h. The experiments proved that the solid residue inevitably remained in supercritical 1-propanol even if the reaction temperature was increased or the reaction time was extended.

The solid residue was characterized by elemental analysis and compared with the cured epoxy resin. Table 2 presents the weight percentages of C, H, O, N, and S. The agreement between the experimental and theoretical values of the cured epoxy resin was excellent. After a degradation time of 1 h, the contents of O and S decreased significantly. Sulfur content of solid residue reduced from 4.06% to 0.89% due to the release of sulfur containing compounds and an evolution of SO_2 [25]. A dehydration reaction



Scheme 2. Scission of diaminodiphenylsulfone units in the epoxy resin.



Scheme 3. Possible degradation mechanism of allylic bonds of the epoxy resin.

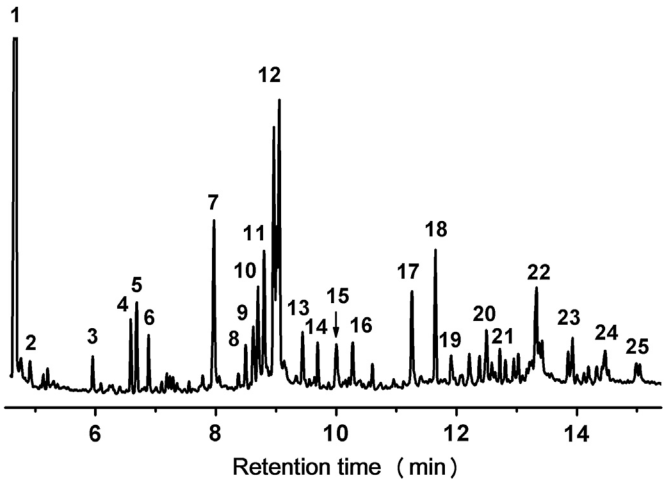
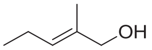
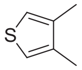
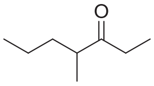
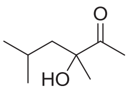
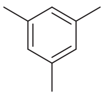
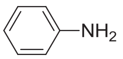
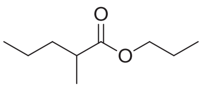
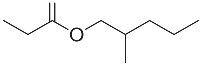
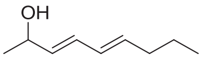


Fig. 12. Total ion chromatogram of the degradation products of TGDDM/DDS resin in supercritical 1-propanol with 1 wt% KOH.

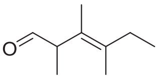
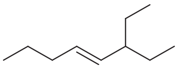
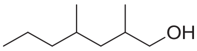
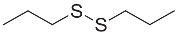
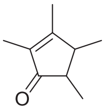
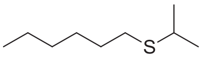
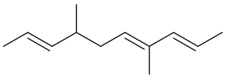
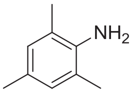
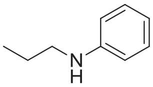
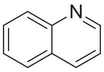
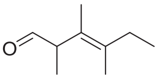
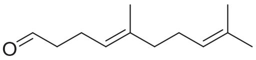
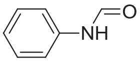
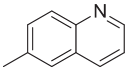
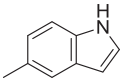
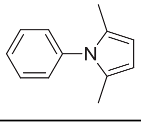
proceeded with elimination of hydroxyl functions, and hydrogen content subsequently decreased from 6.43% to 4.89%. Both the evolution of SO_2 and the dehydration contributed to the oxygen content reduction from 17.01% to 4.67%. The dehydration and the evolution of SO_2 were also confirmed by thermogravimetry–mass spectrometry (TG–MS) of the cured resin. The MS analysis proved

Table 4
Main degradation products of TGDDM/DDS in supercritical 1-propanol under the promotion of KOH at 320 °C and comparison with those obtained without the promotion of KOH.

Peak label	Ret. time (min)	Compounds	Molecular structure	Molar mass (g mol^{-1})	Without KOH
1	4.66	(E)-2-methyl-2-penten-1-ol		100	√
2	4.92	3,4-Dimethylthiophene		112	√
3	5.96	4-Methyl-3-heptanone		128	–
4	6.58	3-Hydroxy-3,5-dimethyl-2-hexanone		144	–
5	6.70	1,3,5-Trimethyl-benzene		120	–
6	6.88	Aniline		93	√
7	7.97	Propyl 2-methylvalerate		158	√
8	8.50	2-Methylpentyl propionate		158	–
9	8.62	Nona-3,5-dien-2-ol		140	–

(continued on next page)

Table 4 (*continued*)

Peak label	Ret. time (min)	Compounds	Molecular structure	Molar mass (g mol^{-1})	Without KOH
10	8.70	2,3,4-Trimethyl-hex-3-enal		140	–
11	8.80	3-Ethyl-4-octene		140	–
12	8.95	2,4-Dimethyl-1-heptanol		144	–
13	9.44	Dipropyldisulfide		150	√
14	9.70	2,3,4,5-Tetramethyl-2-cyclopenten-1-one		138	–
15	10.01	1-[(1-Methylethyl)thio]hexane		160	–
16	10.28	4,7-Dimethyl-decan-2,4,8-triene		164	–
17	11.27	2,4,6-Trimethylaniline		135	–
18	11.65	N-propylbenzenamine		135	√
19	11.91	Quinoline		129	√
20	12.49	2,3,4-Trimethyl-hex-3-enal		140	–
21	12.82	5,9-Dimethyl-4,8-decadienal		180	–
22	13.32	N-phenylformamide		121	–
23	13.90	6-Methylquinoline		143	√
24	14.46	5-Methyl-1H-indole		131	√
25	14.98	2,5-Dimethyl-1-phenyl-1H-pyrrole		171	–

that H_2O (m/e = 18) and SO_2 (m/e = 64) were the major decomposition species in the temperature range 320–400 °C (Fig. 8). The weight percentage of N reduced slightly from 7.92% to 6.95% within 1 h due to the degradability difference between TGDDM and DDS. After thorough theoretical calculation, the weight percentages of N were 6.64, 11.30 and 8.18% for TGDDM, DDS and TGDDM/DDS, respectively. The GC–MS results proved that the degradability of DDS was stronger than that of TGDDM, and the decomposition products of DDS dissolved in 1-propanol. Therefore, the reduction of the DDS content in the solid residue would lead to the minor variation of the weight percentage of N from 8.18 to 6.64%. These agreed well with the actual reduction from 7.92% to 6.95% within 1 h. The weight percentages of C, H, O, N, and S changed slightly when the degradation time varied from 1 to 5 h.

Raman microspectroscopy was applied in the investigation of the solid residue. The Raman spectrum (Fig. 9) showed two broad bands around 1582 and 1358 cm^{-1}, which were generally assigned to carbonaceous materials [26]. The diffuse band at 1582 cm^{-1} clearly reflected the E_{2g} vibrational mode (C—C vibration in the aromatic layers of highly ordered graphite). The band at 1350 cm^{-1} was assigned to A_{lg} vibrational mode of the aromatic layers, and implied the presence of some graphite microcrystals and disordered structure in the solid residue.

X-ray diffraction was also utilized to determine the nature of the solid residue. Fig. 10 represents diffraction spectra of samples obtained at 320 °C after different reaction time. The initial resin had a broad band at 0–9° that suggested a low order in the network. This order was partially maintained after a treatment at 320 °C, but a new broad band appeared at around 12° which was attributed to (002) scatterings of turbostratic carbons [4]. This structure included polyaromatic species which developed by arranging in parallel layers.

The above analysis could be used to explain the formation processes of the undesired solid residue under the reaction temperature and the reaction time. First of all, thermolysis played a key role in decomposing the chemical bonds of the epoxy resin, but also generated aromatic radicals with intensive distribution in the resin. When these adjacent radicals could not be completely terminated to generate organic molecules, their condensation process would induce the polycyclic aromatic hydrocarbons formation [27,28]. Once the polyaromatic structures such as graphite microcrystals formed in the solid residue, they displayed stable chemical properties in supercritical 1-propanol under the reaction temperature.

Table 3 shows the composition and content of the gaseous mixture sampled from the reactor in which TGDDM/DDS was decomposed in supercritical 1-propanol. H_2, CO, CH_4 and C_2–C_3 hydrocarbons were present in the gaseous mixture, and a control reaction without epoxy resin also generated these gas compositions. The H_2 content was remarkably high and its formation was due to 1-propanol dehydrogenation. The contents of SO_2 and H_2S were 6.80 and 12.43 wt%, respectively. The results confirmed the sulfur and oxygen content reduction of the solid residue. The evolution of SO_2 and H_2S were further proved when DDS was held under the similar supercritical conditions, which would be discussed next.

To determine which chemical bonds within TGDDM/DDS resin were broken during the degradation processes, three model compounds were used to conduct tests under the same supercritical conditions. It was found that the concentrations of N,N-diethylbenzenamine and diphenyl methane remained constant during the whole reaction time of 3 h at 340 °C, and the concentration of DDS decreased gradually at 320 °C. Fig. 11 shows the total ion chromatograph (TIC) of the decomposition products of DDS in 1-propanol solution at 320 °C. Aniline was generated by the homolysis of Ph—SO_2Ph bond and subsequent hydrogenation. The alkylation of aniline with 1-propanol yielded N-propylbenzenamine [29]. The hydrogenation of SO_2 and further reaction with 1-propanol produced dipropyldisulfide [30]. Meanwhile, the Guerbet reaction of 1-propanol formed 2-methyl-2-penten-1-ol [31,32]. Therefore, the weakest chemical bonds within the epoxy resin was Ph—SO_2Ph.

On the above basis, a free-radical reaction mechanism was proposed for the depolymerization of TGDDM/DDS resin in supercritical 1-propanol. The elimination of water from the secondary alcohol group was the first reaction when the epoxy resin was heated (Scheme 1). The resulting allylic bonds and Ph—SO_2Ph bond likely experienced homolysis, and the free radicals were saturated by hydrogen transfer from 1-propanol to yield SO_2, aniline, and 4,4′-diaminodiphenylsulfone. The alkylation of aniline with 1-propanol yielded N-propylbenzenamine. The hydrogenation of SO_2 and secondary reactions with propylene produced various sulfur containing compounds such as 2,4-dimethylthiophene, methyl propyl disulfide, dipropyldisulfide (Scheme 2). A possible degradation mechanism for the incorporated diaminodiphenylsulfone units is shown in Scheme 3. These reactions proceeded with homolysis, hydrogenation, as well as cyclization, and yielded aniline, indole, quinoline and their complex derivatives. The evolution of SO_2 and the scission of allylic bonds might correspond to the development of a condensation process which would induce the formation of graphite microcrystals.

Table 5
Composition of the gas mixture sampled from the batch reactor after the decomposition of TGDDM/DDS resin in supercritical 1-propanol with 1 wt% KOH.

Component	General (%)	Without O_2 and N_2 (%)
H_2	88.41	91.28
O_2	0	–
N_2	3.14	–
CH_4	0.88	0.91
CO	1.15	1.19
CO_2	2.02	2.08
C_2H_4	0.31	0.32
C_2H_6	1.71	1.76
C_3H_6	0.95	0.99
C_3H_8	0.86	0.88
H_2S	0.36	0.37
SO_2	0.20	0.21

The effect of KOH additive on chemical depolymerization of the epoxy resin was also investigated. Fig. 12 shows the total ion chromatograph (TIC) of the decomposition products of epoxy resin in 1-propanol solution obtained at 320 °C. The assignment of the main degradation products and the results of the comparison are summarized in Table 4. It was found that aniline and N-propylbenzenamine were invariably present with or without KOH. However, N-phenylformamide and 2,4,6-Trimethylaniline were generated only with KOH. These suggested that the amidation reaction and the Friedel–Crafts reaction of aniline took place in the presence of KOH. In addition, the promotion effect of KOH on the Guerbet reaction was proved by the formation of alcohols with 3 or 4 times more C atoms than that of original alcohol. Table 5 shows the contents of the gaseous mixture after the decomposition of the epoxy resin in supercritical 1-propanol with KOH. Due to the gas formation, the reactor was pressurized even at room temperature. GC analysis showed the gas to be appropriately 88% H_2 and the remainder to be CO_2. Instead of black chars, a white solid was formed. The white solid was apparently potassium carbonate because of good solubility in water and the release of gas upon acidification [24].

Therefore, the outstanding effect of KOH on the decomposition of TGDDM/DDS resin could be explained by a promotion effect of hydrogenation on thermolysis. Upon the addition of KOH, the Guerbet reaction of 1-propanol was promoted to generate more hydrogen. After the thermolysis of chemical bonds in the network of the epoxy resin, the hydrogen scavenged the radicals and prevented the condensation process from producing chars. The hydrogen transfer from supercritical 1-propanol to the resin played an important role in the decomposition reaction.

4. Conclusions

In summary, TGDDM/DDS epoxy resin was successfully decomposed in supercritical 1-propanol. An initial decomposition temperature was about 320 °C for the epoxy resin. The thermolysis of the epoxy resin generated some black solid residue and DDS as well as its fragments including aniline and SO_2. The solid residues contained some graphite microcrystals and disordered structure. The addition of KOH promoted the Guerbet reaction of 1-propanol and more hydrogen was generated. As a result, aniline, N-propylbenzenamine, and their complex derivatives formed. The hydrogenation prevented the formation of the chars. The promotion effect of hydrogenation on thermolysis resulted in the chemical degradation of TGDDM/DDS in supercritical 1-propanol. The application of supercritical 1-propanol in recycling other type of thermosets will be investigated in future work.

Acknowledgments

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References

[1] Pyun E, Sung CSP. Network structure in diamine-cured tetrafunctional epoxy by UV-visible and fluorescence spectroscopy. Macromolecules 1991;24:855–61.

[2] Levchik SV, Camino G, Luda MP, Costa L, Costes B, Henry Y, et al. Mechanistic study of thermal behaviour and combustion performance of epoxy resins. II. TGDDM/DDS system. Polym Degrad Stab 1995;48:359–70.

[3] Pimenta S, Pinho ST. Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook. Waste Manag 2011;31:378–92.

[4] Rose N, Le Bras M, Delobel R, Costes B, Henry Y. Thermal oxidative degradation of an epoxy resin. Polym Degrad Stab 1993;42:307–16.

[5] Pickering SJ. Recycling technologies for thermoset composite materials—current status. Compos Pt A-Appl Sci Manuf 2006;37:1206–15.

[6] Yip HLH, Pickering SJ, Rudd CD. Characterisation of carbon fibres recycled from scrap composites using fluidised bed process. Plast Rubber Compos 2002;31:278–82.

[7] Jiang G, Pickering SJ, Walker GS, Wong KH, Rudd CD. Surface characterisation of carbon fibre recycled using fluidised bed. Appl Surf Sci 2008;254:2588–93.

[8] Luda MP, Balabanovich AI, Zanetti M. Pyrolysis of fire retardant anhydride-cured epoxy resins. J Anal Appl Pyrolysis 2010;88:39–52.

[9] Quan C, Li A, Gao N, Zhang D. Characterization of products recycling from PCB waste pyrolysis. J Anal Appl Pyrolysis 2010;89:102–6.

[10] Jiang G, Pickering SJ, Walker GS, Bowering N, Wong KH, Rudd CD. Soft ionisation analysis of evolved gas for oxidative decomposition of an epoxy resin/carbon fibre composite. Thermochim Acta 2007;454:109–15.

[11] Dang W, Kubouchi M, Yamamoto S, Sembokuya H, Tsuda K. An approach to chemical recycling of epoxy resin cured with amine using nitric acid. Polymer 2002;43:2953–8.

[12] Liu Y, Meng L, Huang Y, Du J. Recycling of carbon/epoxy composites. J Appl Polym Sci 2004;94:1912–6.

[13] Yang P, Zhou Q, Yuan X, Kasteren JMN, Wang Y. Highly efficient solvolysis of epoxy resin using poly(ethylene glycol)/NaOH systems. Polym Degrad Stabil 2012;97:1101–6.

[14] Destais-Orvoen N, Durand G, Tersac G. Glycolysis of epoxide-mine hardened networks II-aminoether model compound. Polymer 2004;45:5473–82.

[15] Liu Y, Liu J, Jiang Z, Tang T. Chemical recycling of carbon fibre reinforced epoxy resin composites in subcritical water: synergistic effect of phenol and KOH on the decomposition efficiency. Polym Degrad Stabil 2012;97:214–20.

[16] Li J, Xu PL, Zhu YK, Ding JP, Xue LX, Wang YZ. A promising strategy for chemical recycling of carbon fiber/thermoset composites: self-accelerating decomposition in a mild oxidative system. Green Chem 2012;14:3260–3.

[17] Braun D, Gentzkow W, Rudolf AP. Hydrogenolytic degradation of thermosets. Polym Degrad Stabil 2001;74:25–32.

[18] Sato Y, Kondo Y, Tsujita K, Kawai N. Degradation behaviour and recovery of bisphenol-A from epoxy resin and polycarbonate resin by liquid-phase chemical recycling. Polym Degrad Stabil 2005;89:317–26.

[19] Jiang G, Pickering SJ, Lester EH, Turner TA, Wong KH, Warrior NA. Characterisation of carbon fibres recycled from carbon fibre/epoxy resin composites using supercritical n-propanol. Compos Sci Technol 2009;69:192–8.

[20] Hyde JR, Lester E, Kingman S, Pickering S, Wong KH. Supercritical propanol, a possible route to composite carbon fibre recovery: a viability study. Compos Pt A-Appl Sci Manuf 2006;37:2171–5.

[21] Pinero-Hernanz R, Garcia-Serna J, Dodds C, Hyde J, Poliakoff M, Cocero MJ, et al. Chemical recycling of carbon fibre composites using alcohols under subcritical and supercritical conditions. J Supercrit Fluids 2008;46:83–92.

[22] Jiang G, Pickering SJ, Lester E, Warrior NA. Decomposition of epoxy resin in supercritical isopropanol. Ind Eng Chem Res 2010;49:4535–41.

[23] Miller JE, Evans L, Littlewolf A, Trudell DE. Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. Fuel 1999;78:1363–6.

[24] Macala GS, Matson TD, Johnson CL, Lewis RS, Iretskii AV, Ford PC. Hydrogen transfer from supercritical methanol over a solid base catalyst: a model for lignin depolymerization. ChemSusChem 2009;2:215–7.

[25] Levchik SV, Camino G, Luda MP, Costa L. Thermal decomposition of 4,4′-diaminodiphenylsulfone. Thermochim Acta 1995;260:217–28.

[26] Dresselhaus MS, Jorio A, Hofmann M, Dresselhaus G, Saito R. Perspectives on carbon nanotubes and graphene Raman spectroscopy. Nano Lett 2010;10:751–8.

[27] Shukla B, Susa A, Miyoshi A, Koshi M. Role of phenyl radicals in the growth of polycyclic aromatic hydrocarbons. J Phys Chem A 2008;112:2362–9.

[28] Comandini A, Malewicki T, Brezinsky K. Chemistry of polycyclic aromatic hydrocarbons formation from phenyl radical pyrolysis and reaction of phenyl and acetylene. J Phys Chem A 2013;116:2409–34.

[29] Li JQ, Andersson PG. Room temperature and solvent-free iridium-catalyzed selective alkylation of anilines with alcohols. Chem Commun 2013;49:6131–3.

[30] Northrop BH, Coffey RN. Thiol-ene click chemistry: computational and kinetic analysis of the influence of alkene functionality. J Am Chem Soc 2012;134:13804–7.

[31] Veibel S, Nielsen JI. On the mechanism of the Guerbet reaction. Tetrahedron 1967;23:1723–33.

[32] Schranck J, Tlili A, Beller M. More sustainable formation of C-N and C-C bonds for the synthesis of N-heterocycles. Angew Chem Int Edit 2013;52:7642–4.