

Chemical Degradation of Amine-cured DGEBA Epoxy Resin in Supercritical 1-Propanol for Recycling Carbon Fiber from Composites*

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Abstract Chemical degradation of diglycidyl ether of bisphenol A (DGEBA) epoxy resin cured with an aliphatic amine in supercritical 1-propanol was investigated under different reaction temperature and time. The combination of GC-MS and LC-MS proved that the epoxy resin was decomposed to five main products including phenol, 4-isopropylphenol, 4-isopropenylphenol, bisphenol A, and 4,4'-(cyclopropane-1,1-diyl)diphenol. The ¹³C-NMR results verified the chemical structures of the degradation products. The change of the products' yield with time was evaluated by an effective means of HPLC. In addition, the GPC analysis confirmed the formation of soluble low molecular weight clusters during the degradation reaction. A possible free-radical reaction mechanism was proposed for chemical depolymerization of the epoxy resin in supercritical 1-propanol. After the homolytic cleavage of the aromatic ether linkages, the resulting bisphenol A biradical either produced 4,4'-(cyclopropane-1,1-diyl)diphenol after intramolecular rearrangement or generated bisphenol A after capturing hydrogen from 1-propanol.

Keywords: Epoxy; Thermosets; Degradation; Recycling.

INTRODUCTION

Chemical degradation of polymer wastes^[1–5] has attracted considerable attention because of its positive environmental impact, the enforcement of legislation with a strict control on landfill and incineration disposal, and a potential recovery of useful compounds. The extensive use of epoxy resin in metal coatings, paints, printed circuit boards, glass fiber or carbon fiber reinforced plastic materials, and structural adhesives has produced an environmental and economic awareness for the need to recycle these materials in a suitable process^[6–9]. Chemical depolymerization of epoxy resin is challenged by its cross-linked network structure, infusibility and insolubility in any solvents^[10]. Epoxy resin is usually formed by the cross-linking reaction of various polyepoxides^[11] with hardeners such as acid anhydrides and polyfunctional amines. Several degradation processes have been reported in order to decompose epoxy resin into low molecular weight compounds. Nitric acid solution was applied successfully for the decomposition of bisphenol F type epoxy resin^[12], but it required an additional neutralization operation before the extraction of organic degradation products from the corrosive solution. On the other hand, effective chemical degradation of bisphenol A type epoxy resin hardened with amines in glycol or 1,4-butanediol at boiling temperature for 14 h suggested that the solvolytic cleavage of ether

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linkages was actually a transesterification reaction^[13]. Highly efficient recycling of anhydride-cured epoxy resin using a poly (ethylene glycol)/NaOH catalytic system at 180 °C in 50 min under atmospheric pressure indicated a combination of ester hydrolysis and transesterification mechanism^[14]. In addition, recent chemical recycling of epoxy resin reinforced composites has exhibited excellent results by solvent-reagents such as methanol, ethanol, 1-propanol and acetone under supercritical or near critical conditions^[15]. Complete elimination of epoxy resin from carbon fiber surface was achieved providing phenolic compounds as the main products at 300–325 °C and 9 MPa with a reaction time of 30–50 min in subcritical water^[16]. The aforementioned processes either required a complicated product separation arising from the high-viscosity of polyols or were difficult to arrive at the conditions such as near critical water. Therefore, novel recycling technologies for epoxy resin should be developed to recover useful degradation products in a sustainable approach that is intrinsically innocuous to live things and the environment.

Hydrogenolysis of aromatic ether linkages provided a new attractive alternative road for chemical degradation of macromolecular materials including the industrial product of epoxy resin and the lignin biopolymer. Hydrogen donors such as tetralin, decalin, 9,10-dihydroanthracene and cyclohexanol were successfully applied to degrade various thermosets including anhydride-cured epoxy resin, phenolic resins, melamine resins and unsaturated polyester^[10, 17]. In addition, hydrogenolysis of phenolic ether linkages led to lignin depolymerization in supercritical methanol after hydrogen was produced from the catalytic methanol reforming^[18–20]. Supercritical alcohol was preferred over supercritical water not only since the critical conditions were less severe but also since hydrogen was *in situ* generated from the alcohol solvent^[21–24]. After complete decomposition of epoxy resin in supercritical isopropanol, Jiang *et al.*^[25] drew a conclusion that thermolysis played a key role in cleaving the chemical bonds of the epoxy resin. Our previous investigation presented a quantitative study on the degradation of epoxy resin by monitoring the change of main products' yields with time^[26]. The promotion effect of hydrogenation on thermolysis was proposed by correlating the elimination of chars with the increase of the hydrogen content. In this paper, bisphenol A type epoxy resin was degraded in supercritical 1-propanol. The quantitative analysis of main degradation products was conducted using HPLC instead of GC because of the thermal sensitivity and high boiling points of bisphenol A^[27–29]. However, an unexpected detection of an intensive peak was obtained during the quantitative analysis. LC-MS further identified that the degradation product has a molecular weight of 226. On the basis that (1) bisphenol A was one of the two components of the epoxy resin and (2) non-aromatic compounds were not measured by an UV detector, an intramolecular rearrangement product of bisphenol A biradical, 4,4'-(cyclopropane-1,1-diyl)diphenol, was assigned to the peak^[30].

The purpose of this paper was to decompose amine-cured DGEBA epoxy resin in supercritical 1-propanol. The main degradation products were identified by GC-MS and LC-MS. The change of the products' yield with time was measured using HPLC to monitor the degradation process. In addition, the degradation products were characterized by ¹³C-NMR and GPC. A possible mechanism combining cleavage of aromatic ether linkages and hydrogenation was proposed for degradation of the epoxy resin in supercritical 1-propanol. The feasibility of recycling carbon fiber from composites made of the epoxy resin was evaluated.

EXPERIMENTAL

Materials

Commercial epoxy resin (diglycidyl ether of bisphenol A (DGEBA), Araldite LY 564) and curing agent (4,4'-methylenebis(2-methylcyclohexylamine), Aradur 2954) were purchased from the Huntsman Advanced Materials Corporation. The epoxy resin for the degradation reaction was prepared by blending DGEBA and the curing agent at a 100:35 weight ratio. After degassing for 40 min, the above blend was poured into a polytetrafluoroethane (PTFE) mold (50 mm × 10 mm × 2 mm), and heated at 80 °C for 1 h before they were cured at 140 °C for 8 h. The reaction solvent, 1-propanol, was obtained from Tianjin Dengfeng Chemical Reagent Corporation (China). The standard samples of phenol, bisphenol A, 4-isopropylphenol, all of them of 99.0 wt% purity, were purchased from the Aladdin Industrial Corporation.

Degradation of the Cured Epoxy Resin

The degradation of amine-cured DGEBA epoxy bar was conducted in a stainless steel autoclave with a volume of 0.5 L. The apparatus was identical to that described in previous report^[26], but was improved in terms of the sampling device for a safer operation. The pressure of the autoclave was detected by a pressure gauge, and the internal temperature was monitored by connecting to a PID controller. A sampling device, made of double needle valves and two stainless steel pipes, was connected with the autoclave by a pipe. The pipe locating between the autoclave and the first needle valve was cooled by a water cooling system. The pipe connecting two needle valves had a volume of 3 mL and was used as a buffer zone for supercritical 1-propanol.

Approximate 3 g of epoxy resin bar and 0.2 L of 1-propanol with or without potassium hydroxide (1 wt%) were placed into the autoclave. The internal temperature of the autoclave was increased and maintained at a series of temperature from 280 °C to 340 °C with a regular interval of 10 K. The epoxy resin was degraded in supercritical 1-propanol for different time ranging from 1 h to 5 h. As supercritical 1-propanol was a homogeneous phase, real-time sampling was performed. After the first needle valve was cautiously switched on, the sample permeated into the buffer zone. Then, the first needle valve was switched off, and 1.5 mL of degradation solution was collected in a sample bottle after switching on the second valve. Both needle valves were closed completely, and the degradation reaction proceeded. After a regular period of time, the repetition of sample extraction was performed. When the degradation reaction was over, the autoclave cooled down to room temperature. GC-MS and LC-MS analyses of the decomposition liquid were carried out. After washing with fresh 1-propanol and drying in an oven at 110 °C for 24 h, the solid residue was weighed. A gas-sampling bag was employed for the capture of the gaseous mixture and subsequent injection into gas chromatography.

Characterization

Fourier transform infrared (FTIR) spectra of the samples were measured on a Nicolet Magna-IR 750 spectrometer employing the usual KBr pellet method. Some fine powder was rubbed off the cured epoxy resin for FTIR. The cross-linking degree of the cured epoxy resin was calculated by comparing the heat with a DSC 200 F3 Maia (Netzsch, Germany). The temperature of the samples was increased from 40 °C to 300 °C at the speed of 5 K·min⁻¹ under nitrogen atmosphere.

The gaseous products were identified and quantified by two gas chromatographies (GC). Model SP-2305 (Beijing Beifenruili Analytic Instrument (Group) Co.) equipped with a 5 Å molecular sieve column and a TCD detector was operated using pure argon as carrier gas. Model GC-1790 (Agilent Technologies Shanghai Analytical Instrument Co. LTD) equipped with a C₁₈ column and an FID detector was run using pure nitrogen as carrier gas. The content of CO₂ was detected through an alkali adsorption method.

An Agilent Model 7890 gas chromatograph coupled with an Agilent Model 5975 quadrupole mass spectrometer was used for the analysis of the degradation solution. An HP-5MS 5% phenyl methyl silox capillary column (30 m × 0.25 mm inner diameter (ID), 0.25 µm film thickness) served as the separation column. The temperatures of the injector port and the detector were 300 °C and 310 °C, setting a gradient temperature from 50 °C to 280 °C for the oven. The flow rate of the carrier gas (helium) was maintained at 1.0 mL·min⁻¹. All MS analyses were implemented 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 without dilution into the gas chromatograph. The library data, NIST08, was applied in the identification of the degradation products.

An Agilent 1100 series equipped with an UV detector, set at 254 nm, and a LC column Agilent C-18 (5 µm particle size, 4.6 × 150 mm) was used to quantitatively analyze degradation liquids. The mobile phase was an acetonitrile-aqueous buffer solution (45:55, V/V) at 40 °C and a flow rate of 0.6 mL·min⁻¹. Degradation samples of 5 µL were injected without dilution. The Agilent HPLC software was employed for data acquisition and integration. The technique produced a good separation of aromatic compounds, and exhibited high sensitivity for phenols and bisphenols. Non-aromatic chemicals were not detected under these conditions.

After distillation, the molecular weight and molecular weight dispersities of the sticky residue free from 1-propanol were measured with an ultimate3000 gel permeation chromatograph (GPC). Three Waters Styragel

columns were employed for separation of the polymer residues, and calibrated against polystyrene standards using tetrahydrofuran (THF) as the mobile phase. The molecular weight detection range was 500–20000. ^{13}C -NMR was performed on a Bruker AVANCE 400 spectrometer using DMSO-d_6 as the solvent. TG-MS experiments (a heating rate of $5\text{ K}\cdot\text{min}^{-1}$ under flow of nitrogen gas) were performed using a STA409PC/MS instrument. Field emission scanning electron images for carbon fiber were taken using a LEO 1530VP microscope with an accelerating voltage of 10 keV.

RESULTS AND DISCUSSION

Characterization of the Epoxy Resin

The cross-linking degree of the cured epoxy resin was evaluated by DSC and FTIR. From the DSC curve of the epoxy resin, little residual exotherm was observed in the cured epoxy resin. After comparing the heat, the level of cross-linking in the cured epoxy resin was found to be 99.2%. In addition, disappearance of the epoxide functions ($972, 914\text{ cm}^{-1}$) and appearance of the hydroxyl functions (3406 cm^{-1}) in FTIR also confirmed the complete cross-linking (Fig. 1). Numerous other peaks were similar to those from the initial epoxy resin.

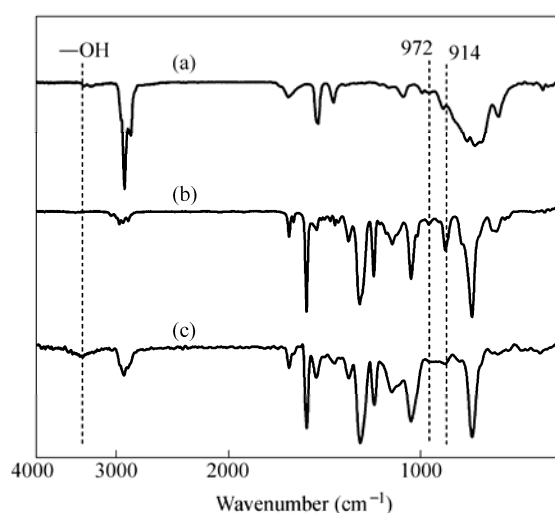


Fig. 1 FTIR spectra of: (a) curing agent (4,4'-methylene-bis-(2-methylcyclohexylamine)), (b) initial epoxy resin (diglycidyl ether of bisphenol A (DGEBA)) and (c) DGEBA epoxy resin cured with the amine

Impact of Temperature

The effect of reaction temperature on chemical degradation of the epoxy resin was evaluated under the following conditions: a reaction time of 60 min, a feedstock ratio of 2 g epoxy resin per 0.2 L 1-propanol, and a series of reaction temperature from $280\text{ }^{\circ}\text{C}$ to $340\text{ }^{\circ}\text{C}$. The epoxy resin bars remained in the original shape, and retained 98.2 wt% to 97.3 wt% of mass in the temperature range from $280\text{ }^{\circ}\text{C}$ to $310\text{ }^{\circ}\text{C}$. However, the epoxy resin bars vanished in the temperature range $320\text{ }^{\circ}\text{C}$ to $340\text{ }^{\circ}\text{C}$. The colors of the degradation liquids darkened from clear, light brown, opaque off-white to deep brown with the temperature rise.

Therefore, temperature played a key role in decomposing the chemical bonds of the epoxy resin, and an initial decomposition temperature was about $320\text{ }^{\circ}\text{C}$ for the epoxy resin under the conditions mentioned above. The chemical bonds of the epoxy resin began to cleave and obvious cracks could be seen below $320\text{ }^{\circ}\text{C}$. With the rise of temperature, the three-dimensional cross-linked network of the epoxy resin partially collapsed. Above the initial decomposition temperature, the resin was completely destroyed to produce soluble low molecular weight clusters and various molecules.

Analysis of the Degradation Products

Figure 2 shows the total ion chromatograph (TIC) of the decomposition products of the epoxy resin after supercritical 1-propanol treatment at 320 °C and 340 °C. As shown in Fig. 2, the decomposition products of the epoxy resin were similar under the temperature of 320 °C and 340 °C. The decomposition products contained four main compounds including phenol, 4-isopropylphenol, 4-isopropenylphenol, and bisphenol A. In addition, 2-methylpent-2-en-1-ol and 3-hydroxy-2-methylpentanal were also present in the 1-propanol solution. A negligible level of phenolic compounds such as *o*-cresol, 2-ethylphenol, and 2-allyl-4-methylphenol was detected.

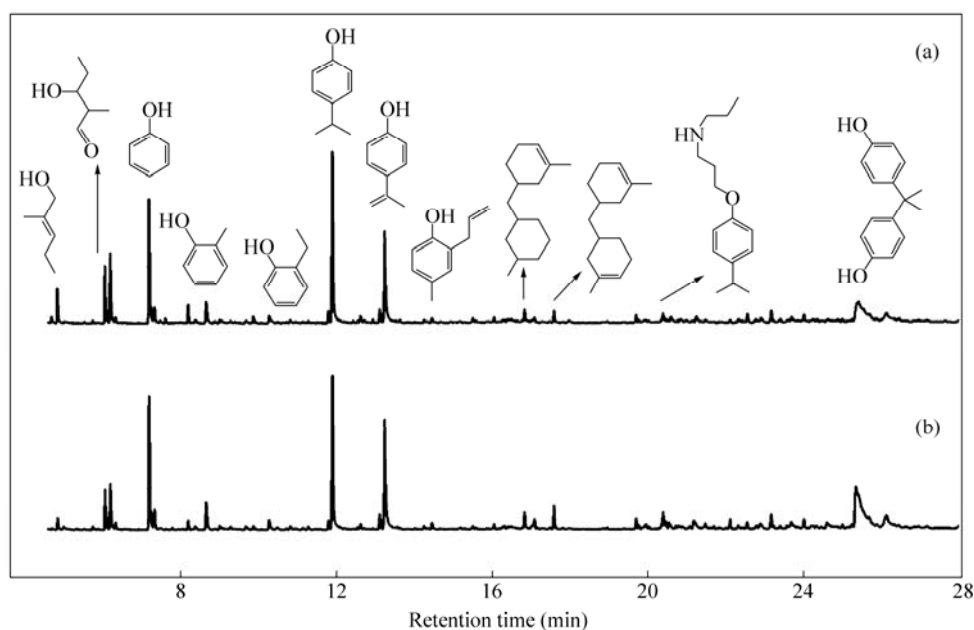


Fig. 2 Total ion chromatograms of the degradation products of the epoxy resin degraded in supercritical 1-propanol at (a) 320 °C and (b) 340 °C for 60 min

The epoxy resin disappeared after a reaction time of 60 min at 320 °C, but vanished after 20 min at 340 °C. The increase of the apparent degradation rate with the temperature rise agreed well with the Arrhenius rate laws. In order to monitor the degradation process in an accurate manner, the quantitative analysis of the decomposition products was performed by taking 1.5 mL of decomposition products sample regularly from the reactor for HPLC. Four main products including bisphenol A, phenol, 4-isopropenylphenol and 4-isopropylphenol were identified according to the retention time of the corresponding standard samples (Fig. 3). However, an unexpected detection of an intensive peak is obtained using HPLC.

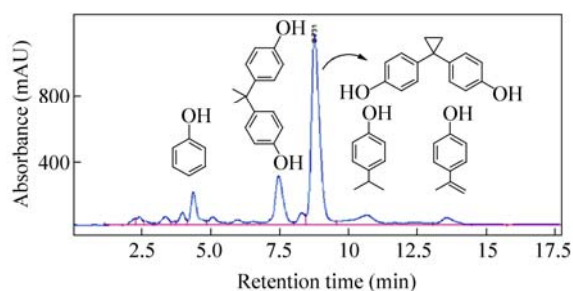


Fig. 3 HPLC chromatogram of a sample of the degradation mixture

An intramolecular rearrangement product of bisphenol A biradical, 4,4'-(cyclopropane-1,1-diyl)diphenol, was assigned to the unexpected peak for three reasons. First, bisphenol A biradical could be generated during the degradation of the epoxy resin. Bisphenol A biradical was formed in the pyrolysis of polycarbonate and its kinetic lifetime was of order of hours^[30]. It was reasonable to speculate that a simple homolytic cleavage of aromatic ether linkages in the epoxy resin could produce the bisphenol A biradical. The biradical generated bisphenol A after hydrogenation, or produced 4,4'-(cyclopropane-1,1-diyl)diphenol after hydrogen transfer within the biradical. Then, LC-MS results indicated the presence of 4,4'-(cyclopropane-1,1-diyl)diphenol. An intensive peak at m/z 225 was observed using detection mode of selected ion monitoring (SIM) (Fig. 4). 4,4'-(Cyclopropane-1,1-diyl)diphenol, with a molecular weight of 226, predominantly formed de-protonated ions $[M-H]^-$ in negative ionization mode. Bisphenol A actually generated de-protonated ions $[M-H]^-$ with a molecular weight of 227. Therefore, the intensive peak was assigned to 4,4'-(cyclopropane-1,1-diyl)diphenol. Finally, the intramolecular rearrangement product of bisphenol A biradical was proven by ^{13}C -NMR analysis. The chemical structures of 4,4'-(cyclopropane-1,1-diyl)diphenol and bisphenol A were similar for they both contained bisphenol unit.

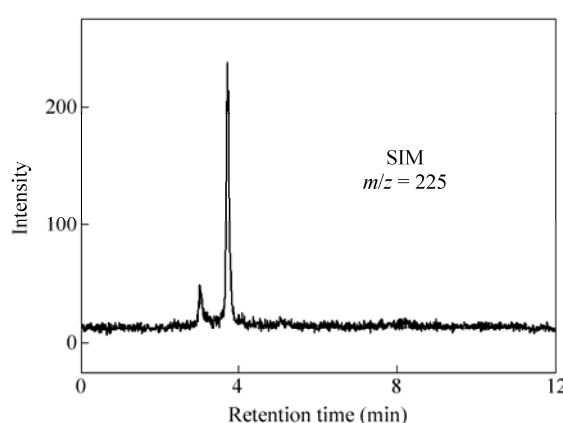


Fig. 4 SIM chromatogram of a sample of the degradation solution

Figure 5 presents the ^{13}C -NMR spectra of the initial DGEBA^[31] and the decomposition products. Various resonance peaks were assigned to the carbons as marked in the inset chemical structure. The assignment of the resonance peaks is specified in Table 1. For the initial DGEBA (spectrum A), the resonances at $\delta = 157$, 143, 128 and 114 were ascribed to protonated and non-protonated aromatic carbons, respectively. The resonances at $\delta = 72$, 71 and 69 were assigned to the aliphatic carbons linking with oxygen, and the resonances at $\delta = 50$ and 44 were attributed to the epoxide rings. In addition, the resonance at $\delta = 42$ was the signal of the quaternary carbons and the resonance at $\delta = 31$ was assigned to methyl groups. For the standard sample of bisphenol A (spectrum B), the resonances at $\delta = 155$, 142, 128 and 115 were signals of protonated and non-protonated aromatic carbons, respectively. The resonances at $\delta = 42$ and 31 were ascribed to the quaternary carbons and the methyl groups. For the decomposition products (spectra C and D), the typical resonance peak of bisphenol A was observed due to the presence of 4,4'-(cyclopropane-1,1-diyl)diphenol and bisphenol A. On the other hand, some weak resonance peaks at $\delta = 158$, 143 and 114 were similar to those of the initial DGEBA. The resonances at $\delta = 71$ and 69 were not observed due to the elimination of water from the secondary alcohol group. Various resonance peaks from $\delta = 10$ to 70 were assigned to aliphatic carbons, which might be the products of the Guerbet reaction of 1-propanol. The ^{13}C -NMR analysis proved the chemical structure of the residue. Instead of bisphenol A biradical or dienone analogues, 4,4'-(cyclopropane-1,1-diyl)diphenol might result in the ^{13}C -NMR spectra. The change of the products' yield with time was discussed in the following parts.

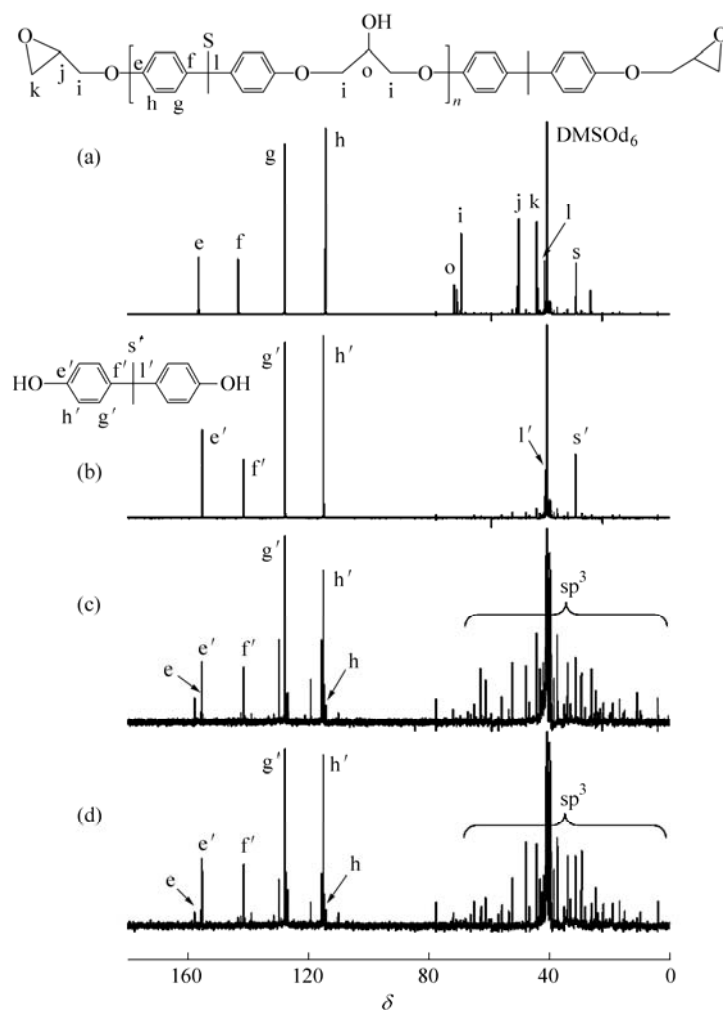


Fig. 5 ^{13}C -NMR spectra of: (a) initial epoxy resin, (b) bisphenol A, the products after depolymerization at 320 °C for (c) 1 h and (d) 2 h

Table 1. Assignment of the ^{13}C chemical shifts for the initial DGEBA, bisphenol A, and the decomposition products

Peak label	Chemical shift δ	Type of carbon
e	157	C—O (aromatic, DGEBA)
e'	155	C—OH (aromatic, bisphenol A)
f	143	Tertiary carbon (aromatic, DGEBA)
f'	142	Tertiary carbon (aromatic, bisphenol A)
g, g'	128	Aromatic CH (DGEBA, bisphenol A)
h	114	Aromatic CH (DGEBA)
h'	115	Aromatic CH (bisphenol A)
o	72, 71	C—O (aliphatic, DGEBA)
i	69	C—O (aliphatic, DGEBA)
j	50	Epoxide methyldiene CH (DGEBA)
k	44	Epoxide methylene CH_2 (DGEBA)
l, l'	42	Quaternary carbon (DGEBA, bisphenol A)
s, s'	31	Methyl group CH_3 (DGEBA, bisphenol A)

At 320 °C, the content of 4,4'-(cyclopropane-1,1-diyl)diphenol was much higher than that of bisphenol A and its fragments such as phenol, 4-isopropenylphenol and 4-isopropylphenol (Fig. 6). The yield of

4,4'-(cyclopropane-1,1-diyl)diphenol increased rapidly to its maximum of 19.85 wt% after 3 h, and reached 21.60 wt% gradually from 3 h to 5 h. The yield of bisphenol A rose promptly to 6.52 wt% after 3 h, and became 8.12 wt% after 5 h. The yields of 4-isopropylphenol, phenol and 4-isopropenylphenol increased monotonously during the reaction time of 5 h, and reached the maximum of 3.64 wt%, 2.02 wt%, and 1.88 wt%, respectively.

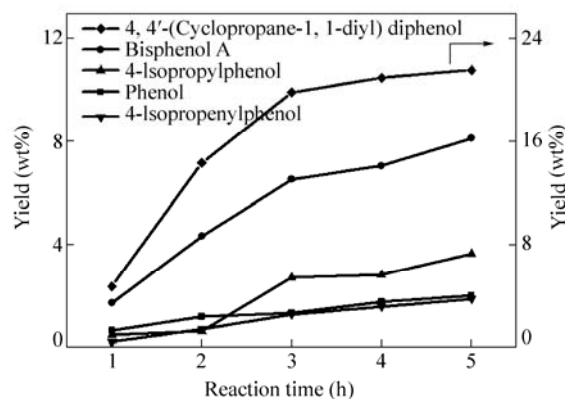


Fig. 6 Yields of main degradation products versus the reaction time at 320 °C

A series of consecutive reactions took place during the degradation of epoxy resin. Some degradation products were intermediates, and others were final products. The yields of the intermediates reduced with the increase of reaction steps. To overcome the decreases in the total yield, step-economic processes were pursued in synthetic chemistry^[32]. During the degradation of amine-cured DGEBA epoxy resin, biphenol A biradicals were generated after the homolytic cleavage of aromatic ether linkages. With lower energies, 4,4'-(cyclopropane-1,1-diyl)diphenol was formed because of the intramolecular rearrangement of biphenol A biradical. On the other hand, biphenol A biradical experienced a more reaction step of hydrogenation and produced bisphenol A. Therefore, the yield of 4,4'-(cyclopropane-1,1-diyl)diphenol was much higher than that of bisphenol A. In addition, thermal fragment of bisphenol A produced 4-isopropenylphenol. Bisphenol A is cleaved to 4-isopropylphenol under hydrogenation conditions^[33]. As a result, the yield of bisphenol A was much higher than its fragments including 4-isopropenylphenol, 4-isopropylphenol, and phenol. At the later stage, 4-isopropylphenol was preferred over 4-isopropenylphenol because of hydrogenation of 4-isopropenylphenol.

At 340 °C, the yield of 4,4'-(cyclopropane-1,1-diyl)diphenol was also much higher than that of bisphenol A and its fragments (Fig. 7). The yield of 4,4'-(cyclopropane-1,1-diyl)diphenol grew rapidly to its maximum of 24.38 wt% after 40 min, and remained the constant amount from 40 min to 60 min. The yield of bisphenol A increased monotonously to 6.70 wt% after 60 min. The yields of 4-isopropylphenol, phenol, and 4-isopropenylphenol reached the maximum of 4.54 wt%, 1.98 wt% and 2.08 wt%, respectively.

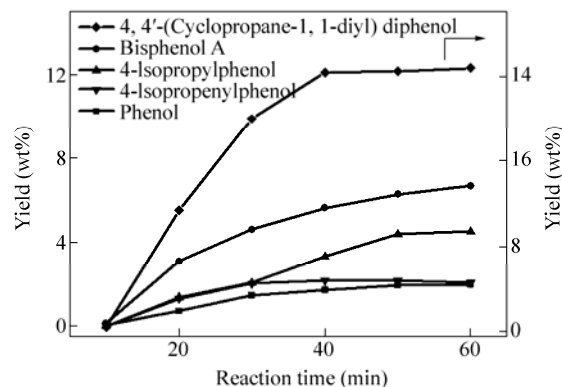


Fig. 7 Yields of main degradation products versus the reaction time at 340 °C

In addition to organic molecules, soluble low molecular weight clusters were separated from the degradation solution and accounted for about 10 wt% of the whole original cured resin after centrifugation (a rotational speed of 8000 r/min) and desiccation. The initial epoxy resin and the decomposition products were evaluated by GPC to determine their molecular weight distribution (MWD). From the GPC traces (Fig. 8), the initial epoxy resin consisted of narrow molecular weight distribution, polydispersive index (PDI) 1.01, ranging from 624 Da to 1192 Da, and the decomposition products had a wider molecular weight distribution, polydispersive index 1.38, ranging from 624 Da to 5120 Da. Furthermore, the initial resin possessed an intensive molecular weight distribution around 624 Da that corresponded to 1 repeat unit in diglycidyl ether of bisphenol A (DGEBA). After a treatment for 1 h or 2 h, the decomposition products also had the molecular weight distribution around 624 Da. These results implied that the epoxy resin was destroyed to soluble low molecular weight clusters in addition to 4,4'-(cyclopropane-1,1-diyl)diphenol, bisphenol A, and its fragments.

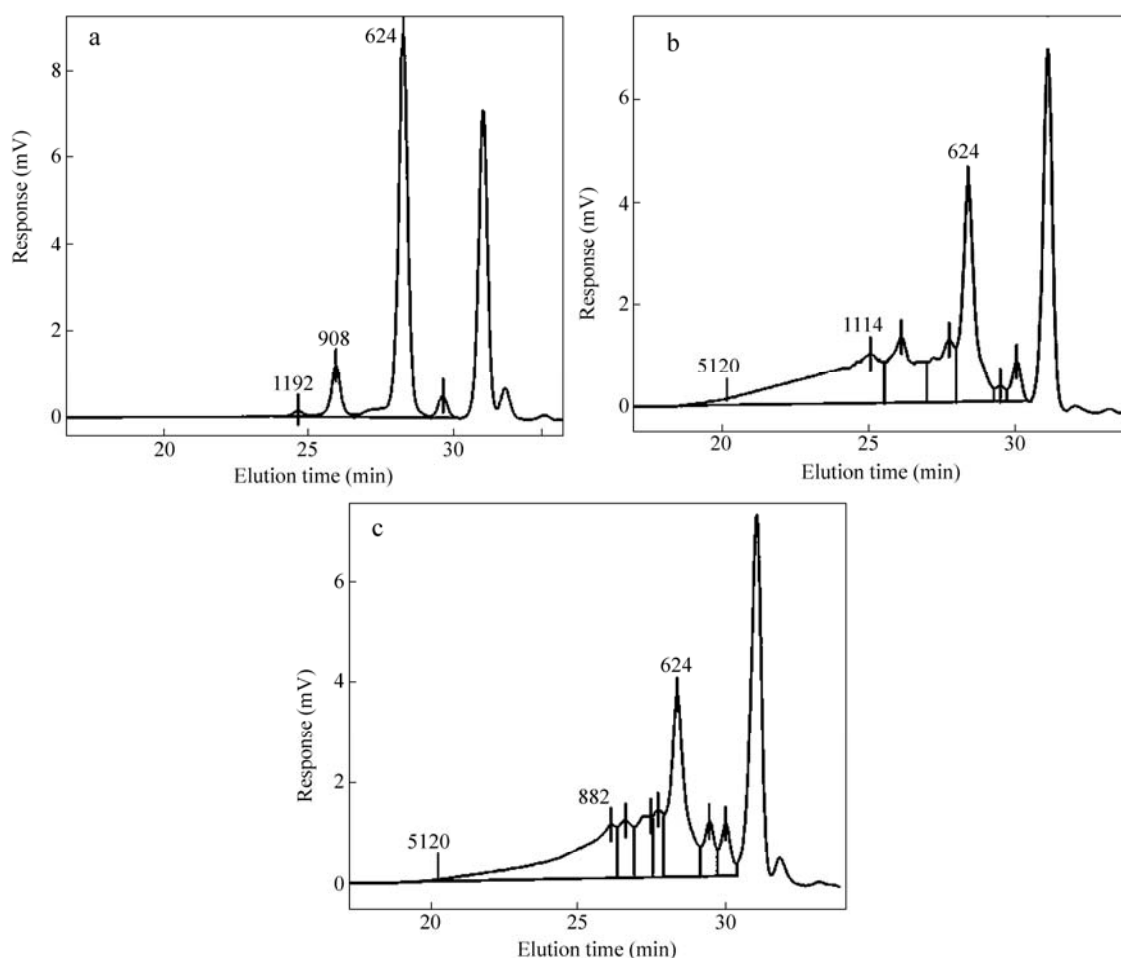


Fig. 8 The GPC traces of (a) initial epoxy resin and the products after depolymerization at 320 °C for (b) 1 h, (c) 2 h

Degradation Mechanism: Homolysis and Hydrogen Transfer

The thermal properties of the epoxy resin were investigated by simultaneous thermogravimetry-mass spectrometry (TG-MS). The mass analysis revealed that H_2O ($m/e = 18$) and phenol ($m/e = 94$) were the major decomposition species in the temperature range of 320 °C to 450 °C (Fig. 9). Since the initial decomposition temperature was 320 °C, it was reasonable to conclude that the elimination of water from the secondary alcohol group proceeded in the epoxy resin under the reaction conditions.

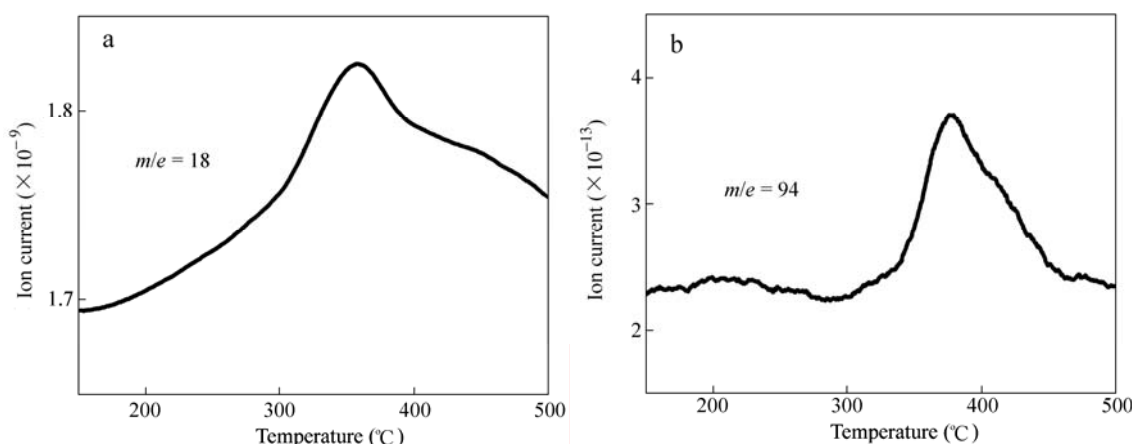


Fig. 9 Temperature-dependent mass spectra of the cured epoxy resin at (a) m/e 18 and (b) m/e 94

To pinpoint which chemical bonds were broken during the degradation process, three model compounds were used to conduct tests under the same supercritical conditions. It was found that the concentrations of *N,N*-dimethylcyclohexanamine and ethoxybenzene remained the same during the whole reaction time of 3 h at 340 °C, suggesting that cyclohexane unit was preserved in the epoxy resin. However, the concentration of bisphenol A decreased gradually, indicating the cleavage of the chemical bond of $\text{Ph-C}(\text{CH}_3)_2\text{Ph}$ under the reaction conditions. Table 2 presents bond dissociation enthalpies (BDE) of various phenoxy derivatives^[34]. The bond dissociation enthalpy of $\text{PhO-CH}_2\text{C}_2\text{H}_5$, 211.8 $\text{kJ}\cdot\text{mol}^{-1}$, was about 20% lower than that of $\text{PhO-C}_2\text{H}_5$. These data could be used to explain the reason why 4,4'-(cyclopropane-1,1-diyl)diphenol and bisphenol A were generated from the epoxy resin, but the concentration of ethoxybenzene remained no change. $\text{PhO-CH}_2\text{C}_2\text{H}_3$ unit within the epoxy resin was formed due to the elimination of water from the secondary alcohol group, and the reduced bond dissociation enthalpy made it possible to produce bisphenol A biradicals from the epoxy resin.

Table 2. Bond dissociation enthalpies (BDE) of various phenoxy derivatives ($\text{kJ}\cdot\text{mol}^{-1}$) at 298 K^[34]

Compounds	BDE ($\text{kJ}\cdot\text{mol}^{-1}$)	Compounds	BDE ($\text{kJ}\cdot\text{mol}^{-1}$)
PhO-CH_3	273.8	$\text{PhO-C}_2\text{H}_5$	272.5
PhO-CH_3	274.6	$\text{PhO-C}_2\text{H}_5$	267.9
PhO-CH_3	275.4	$\text{PhO-C}_2\text{H}_5$	285.9
<i>o</i> - $\text{CH}_3\text{OPhO-CH}_3$	258.7	$\text{PhO-C}_2\text{H}_3$	322.3
<i>o</i> - $\text{CH}_3\text{OPhO-CH}_3$	257.4	$\text{Ph-OC}_2\text{H}_3$	321.9
<i>p</i> - $\text{CH}_3\text{OPhO-CH}_3$	257.0	PhO-Ph	334.0
<i>o</i> - HOPhO-CH_3	244.9	$\text{PhO-CH}_2\text{C}_2\text{H}_3$	211.8
<i>p</i> - HOPhO-CH_3	265.8	$\text{PhO-CH}_2\text{Ph}$	233.6

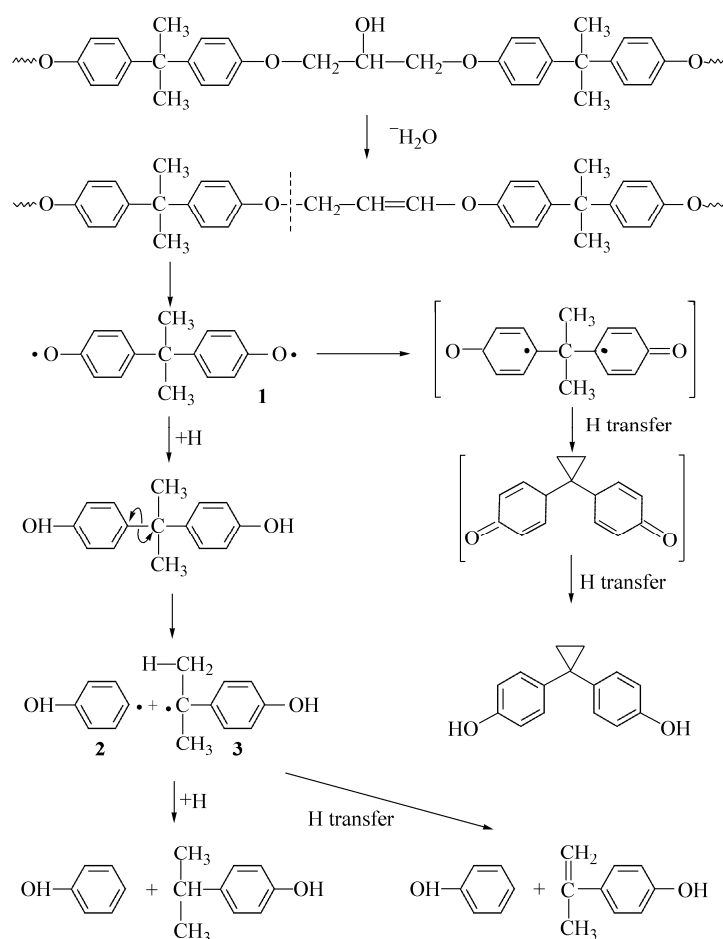
Table 3 shows the contents of the gaseous mixture obtained from the reactor in which the epoxy resin was decomposed in supercritical 1-propanol. It could be seen that the depolymerization of the epoxy resin in supercritical 1-propanol produced H_2 , CO , CH_4 and $\text{C}_2\text{-C}_3$ hydrocarbons. The contents of H_2 and CO_2 were remarkably high and those of CO , CH_4 and $\text{C}_2\text{-C}_3$ hydrocarbons were insignificant. A control reaction without the epoxy resin generated a similar gas mixture. Thus, the formation of the gases might be due to 1-propanol dehydrogenation and subsequent reactions.

On the above basis, a free-radical reaction mechanism is proposed in Scheme 1 for the degradation of the epoxy resin in supercritical 1-propanol. The elimination of water from the secondary alcohol group was the first reaction when the epoxy resin was heated^[10, 26]. The resulting allylic bonds, aromatic ether linkages, experienced homolytic cleavage. The free radical **1** was saturated by active hydrogen from 1-propanol to yield bisphenol A. The intramolecular hydrogen transfer of biphenol A biradical generated 4,4'-(cyclopropane-1,1-diyl)diphenol. Then bisphenol A also underwent homolysis and formed free radicals (**2** and **3**). The free radical **2** could capture

hydrogen from the neighboring methyl in the free radical **3** to generate phenol and 4-isopropenylphenol. On the other hand, the free radicals (**2** and **3**) were saturated by hydrogen transfer from 1-propanol to yield phenol and 4-isopropylphenol.

Table 3. Composition of the gas mixture after the decomposition of the epoxy resin in supercritical 1-propanol

Component	General (%)	Without O ₂ and N ₂ (%)
H ₂	5.02	40.06
O ₂	1.42	—
N ₂	86.05	—
CH ₄	0.40	3.20
CO	0.45	3.61
CO ₂	5.56	44.31
C ₂ H ₄	0.05	0.38
C ₂ H ₆	0.33	2.67
C ₃ H ₆	0.28	2.26
C ₃ H ₈	0.44	3.50



Scheme 1 Possible degradation mechanism of bisphenol A type epoxy resin in supercritical 1-propanol

Impact of Potassium Hydroxide Additive

The effect of KOH additive on chemical degradation of the epoxy resin was also investigated. Figure 10 shows the total ion chromatogram (TIC) of the decomposition products of the epoxy resin at 320 °C for 1 h. The degradation products contained phenol, 4-isopropylphenol and the corresponding derivatives. Table 4 shows the

contents of the gaseous mixture after degradation of the epoxy resin in supercritical 1-propanol under the promotion of KOH. The H_2 mole fraction was up to 89%.

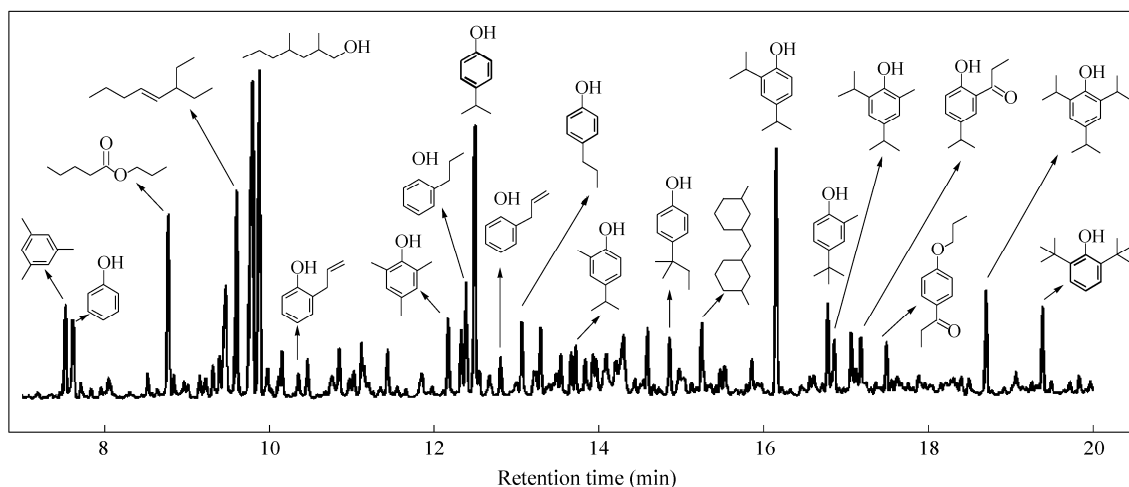


Fig. 10 Total ion chromatogram of the degradation products of epoxy resin in supercritical 1-propanol under the promotion of KOH (1 wt%)

The KOH promoted degradation reaction was conducted in the batch reactor at 320 °C for 60 min.

Table 4. Composition of the gas mixture after the degradation of the epoxy resin in supercritical 1-propanol under the promotion of KOH (1 wt%)

Component	General (%)	Without O_2 and N_2 (%)
H_2	89.12	92.34
O_2	0	—
N_2	3.48	—
CH_4	0.86	0.89
CO	0.88	0.92
CO_2	2.03	2.10
C_2H_4	0.26	0.27
C_2H_6	1.64	1.66
C_3H_6	0.94	0.97
C_3H_8	0.81	0.84

Based on the results, KOH promoted the degradation of the epoxy resin because more hydrogen was generated. The elimination of water from the secondary alcohol group proceeded when the epoxy resin was heated. The resulting allylic bonds likely experienced homolysis, and the formed allyloxybenzene underwent the Claisen rearrangement reaction to generate *o*- or *p*-substituted phenol. The free radicals (**2** and **3**) were saturated by hydrogen transfer from 1-propanol to yield phenol and 4-isopropylphenol. Then, under the action of KOH, the electrophilic substitution of phenol and 4-isopropylphenol proceeded to produce their derivatives.

Therefore, the outstanding effect of supercritical 1-propanol on the degradation of the epoxy resin could be explained by the combination of homolysis and hydrogenation. After the homolysis of aromatic ether linkages in the network of epoxy resin, the radicals were terminated by hydrogen from supercritical 1-propanol. The hydrogen transfer played a key role in the degradation reaction.

Finally, the recycling of carbon fibers from composites made of the epoxy resin and carbon fibers was investigated. Figure 11 shows SEM images of the recycled carbon fibers. From the SEM images, the recycled fibers appeared to be basically free from the epoxy resin and had a clean surface. There was no obvious reduction in diameter or surface scratches on the recycled fibers, suggesting that the carbon fibers were recycled with little damage. The tensile strength of the recycled fibers amounted to 3.47 GPa. This was roughly the same value which the carbon fibers had before they were combined with the epoxy resin.

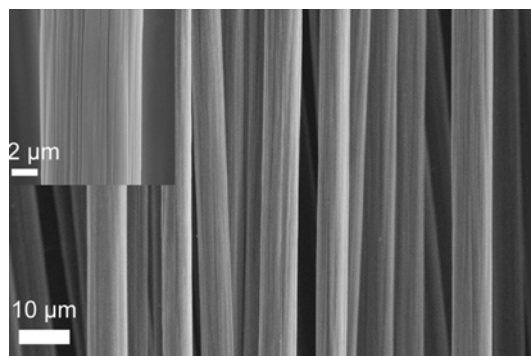


Fig. 11 SEM images of the recycled carbon fiber (inset, higher magnification)

CONCLUSIONS

In summary, amine-cured DGEBA epoxy resin was successfully degraded in supercritical 1-propanol. An initial degradation temperature was about 320 °C for the epoxy resin. After complete degradation five main compounds were obtained and their yields followed the order: 4,4'-(cyclopropane-1,1-diyl)diphenol > bisphenol A > phenol, 4-isopropenylphenol, 4-isopropylphenol. A possible reaction mechanism combining intramolecular rearrangement and hydrogenation was proposed. After the homolytic cleavage of aromatic ether linkages, the resulting bisphenol A biradical either became 4,4'-(cyclopropane-1,1-diyl)diphenol after intramolecular rearrangement or generated bisphenol A after hydrogenation. The addition of KOH promoted the Guerbet reaction of 1-propanol and more hydrogen was generated. As a result, phenol, 4-isopropylphenol, and their complex derivatives formed. The hydrogen transfer to the resin played an important role in the degradation reaction. Supercritical 1-propanol has many potential benefits including mild reaction conditions, the recovery of 1-propanol and phenol derivatives, and *in situ* generation of hydrogen. The catalytic conversion of phenol derivatives into alkanes in supercritical 1-propanol will be investigated in future work.

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