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Research Article

Decomposition of Epoxy Model Compounds in Near-Critical Water

Two tpyes of epoxy resin model compounds, one containing an ether bond and bisphenol-A structure (compound I) and the other comprising ether and tertiary amine bonds (compound II), were prepared and then decomposed in near-critical water (NCW). In the case of model compound I, at low temperatures the water molecules behave as nucleophilic reagent reacting with the terminal ether group of the model compound. When the temperature is increased, the middle ether bond of the model compound molecule can be broken down. As to model compound II, at lower temperatures, cleavage of the ether bond happens more easily than that of the tertiary amine bond because of higher positive charge density centered at the carbon atom in the ether group. At higher temperatures, the energy required to break down the ether bond is reduced dramatically after being protonated by H^+, and therefore, the bond can be cleaved more readily than the tertiary amine bond. 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.

1   Introduction

The increasing production and applications of epoxies [1] and their composites [2, 3] have attracted much attention to the recycling of these epoxy wastes which are difficult to dispose due to their cross-linked structures. Several technologies have been developed to dispose epoxies and other polymer wastes [4]. For example, relatively inexpensive and simple mechanical treatment of the polymer wastes by crushing and milling may provide short fibers with relatively poor mechanical properties which can be used as filler or reinforcement materials [5, 6]. Pyrolysis processes allow for the recovery of long fibers, however, disadvantages are reduced mechanical properties and oxidation of the polymers [7, 8].

In recent years, chemical recycling is emerging as a promising approach to convert epoxy wastes to their monomers or petrochemical feedstock [9–11]. Supercritical fluids (SCFs)

and near-critical fluids (NCFs) have been considered as potential media since they possess an intriguing combination of properties such as low viscosity, high mass transport coefficients, high diffusivity, and solvation power [12–14]. Solvolytic processes such as methanolysis, glycolysis, hydrogenolysis, and alcoholysis [15–18] have been reported to decompose epoxy resin into its original monomers. However, the potential toxicity of solvents and high-cost separation of the solvents from the chemical feedstock are main problems.

Supercritical water (SCW), i.e., water above its critical point ($T_c = 373.946\,°C$, $P_c = 22.064$ MPa) [19], and near-critical water (NCW) or subcritical water, i.e., water at 250–300 °C [20], turn out to be alternative candidates for reasons that water is safe, non-toxic, readily available, inexpensive, and environmentally benign. Convenient post-reaction separation of water and products can also be obtained by simply reducing the system temperature based on the fact that water is poorly miscible with most organic products at lower temperatures [12, 21–23].

Employing SCW and NCW as media for biomass processing and chemical synthesis in the presence of acid or base catalysts or transition metal salts has been reported [24–27]. Some research on chemical recycling of plastics using SCW and NCW has also been conducted. It was found that the condensation polymers, i.e., polyurethane, Nylon 6, and polycarbonates,

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could be readily decomposed into their monomers by hydrolysis in SCW or NCW [23, 28, 29]. Other polymers such as phenol resin, however, are relatively difficult to be decomposed, and proper agents are needed to accelerate decomposition [30].

Compared to SCW, NCW requires lower temperature and thus reduces the subsequent operation cost, while it maintains a high ion constant (K_w; $K_w = $[H$^+$][OH$^-$]) and a low dielectric constant to serve as a suitable solvent and reaction medium for disposing epoxy wastes. In previous work, we studied the decomposition of epoxy in NCW without any additives and the effects of parameters including reaction temperature, reaction time, feedstock ratio, and pressure on the decomposition rate; in addition, a kinetic equation was established [31].

To further understand the decomposition mechanisms of cured epoxy resin in NCW and to optimize the operating parameters for further controllable recycling of epoxy wastes, two

types of epoxy resin model compounds, one containing bisphenol-A structure and the other ether and tertiary amine bonds, are synthesized and characterized (Fig. 1). Then these two model compounds are decomposed in NCW under different experimental conditions. The products are identified qualitatively and quantitatively by GC-MS. Decomposition mechanisms of the model compounds in NCW are proposed.

2 Experimental

2.1 Materials

Bisphenol-A (BPA) was provided by Tianjin Guangfu Fine Chemical Research Institute and phenyl glycidyl ether (GPE) by Tokyo Chemical Industry Co. Ltd., Japan. *N,N'*-Dimethyl-
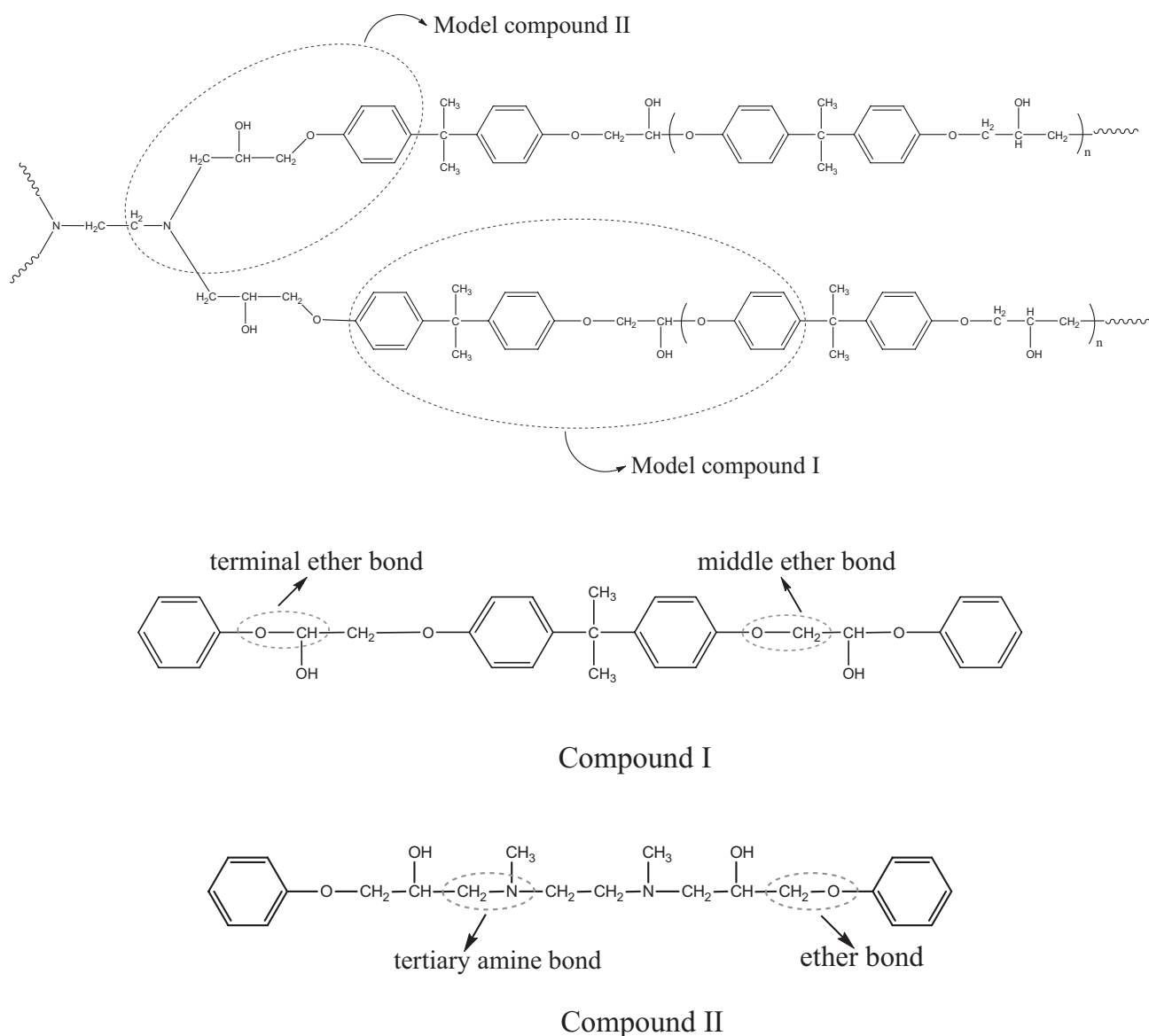

Figure 1. Chemical structures of epoxy model compounds I and II and characteristic functional groups in model compound I and II.

ethylenediamine was purchased from Jingyan Chemicals (Shanghai) Co., Ltd.

2.2 Synthesis and Characterization of Epoxy Model Compounds

Model compound I was synthesized from BPA and GPE under NaOH catalysis. BPA (3.224 g) was added to 15 mL 10 wt % NaOH aqueous solution and heated to 100 °C to get a clear solution under magnetic stirring. Then 4.2 mL GPE was added drop-wise to the solution above. The clear solution was observed to become cloudy instantly after the addition of GPE. The reaction was terminated after 2 h and an oil-milky liquid product was obtained. The oily product was rinsed several times with hot water (80 °C) until the washing solution turned to neutral pH. Finally, the product was put into a conventional vacuum oven at 50 °C for 12 h to get rid of the water. A clear and colorless jelly product was finally obtained.

Model compound II was synthesized according to [32]. Briefly, 5.0 mL N,N'-dimethyl-1,2-ethanediamine (NND) was put into a flask equipped with reflux condenser and magnetic stirring. The system was deoxygenated by purging with nitrogen gas for half an hour. BPA was added drop-wise to the flask within 1 h when NND began to reflux. The reaction was completed within another hour. The whole reaction was conducted in an inert atmosphere. In the end, a dark-brown oily liquid product was obtained.

Fourier transform infrared spectrometry (FTIR), proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, and mass spectrometry (MS) were employed to characterize the structure of the model compounds. The samples for FTIR were prepared by placing the model compound between two KBr plates to form an even film for an IR spectrum. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 MHz using CDCl$_3$ as the solvent. Electrospray ionization mass spectrometry (ESI-MS) of the model compound was performed by solving the model compound in methanol using a positive ESI mode.

2.3 Decomposition of Epoxy Model Compounds in NCW and Analysis of the Products

Decomposition of epoxy model compounds in NCW was conducted in a stainless-steel batch autoclave (5.0 cm inner diameter, 20 cm length) with a volume of 100 cm^3, consisting of a body and a fastening cap connected to a pressure gauge. A round salt bath furnace heated the reactor to a set temperature. The experiment was conducted as follows. First, the model compound was put into the reactor along with 10 mL distilled water. Then, the reactor was sealed, heated in an electric furnace to a set temperature for a defined time, and cooled to ambient temperature in a cold-water bath. The final pressure of the reactor was recorded. The resulting decomposition solution was transferred to a beaker and extracted using ethyl acetate. The supernatant fluid was kept for GC-MS characterization.

Model compound I was decomposed in NCW at 265 °C and 285 °C for 30, 45, 60, 90, and 120 min, respectively. Tab. 1 sum-

Table 1. Decomposition parameters for model compound I in NCW.

Temperature [°C]	Reaction time [min]	Final pressure [MPa]
265	30	3.2
265	45	3.7
265	60	3.8
265	90	3.9
265	120	4.0
285	30	4.8
285	45	4.8
285	60	5.7
285	90	6.0
285	120	6.2

marizes decomposition temperature, reaction time, and the recorded final pressure of the reactor.

For decomposition of model compound II, the temperatures were set at 285, 305, and 325 °C. The reaction time at each temperature was 30, 60, 90, 120, and 150 min, respectively. Tab. 2 presents decomposition temperature, reaction time, and recorded final pressure of the reactor.

Table 2. Decomposition parameters for model compound II in NCW.

Temperature [°C]	Reaction time [min]	Final pressure [MPa]
285	30	4.7
285	60	5.5
285	90	5.5
285	120	5.5
285	150	5.7
305	30	6.1
305	60	6.5
305	90	7.0
305	120	7.0
305	150	7.0
325	30	7.0
325	60	8.7
325	90	8.7
325	120	8.7
325	150	8.7

The decomposition products were identified qualitatively and quantitatively by GC-MS (Agilent 5973N). Each sample (1 µL) was injected manually in splitless mode. The sample was carried into a DB-5MS fused-silica capillary column (30 m,

0.25 mm inner diameter, 0.25 µm film thickness) using helium as carrier gas at a flow rate of 10 mL min⁻¹. The column was held at 50 °C initially for 5 min, then programmed to a final temperature of 280 °C at a heating rate of 20 °C min⁻¹, and held at that temperature to give a total run time of 19.5 min. The column effluent was introduced into the ion source at 230 °C. The ions were generated by a 70-eV electron beam at an ionization current of 2.0 mA, and the spectra were recorded in the mass range of 15–400 amu.

3 Results and Discussion

The molecular structure of the model compounds synthesized was confirmed by FTIR, ¹H NMR, and MS (see Supporting Information).

3.1 Decomposition Products of Epoxy Model Compound I in NCW at Different Temperatures and Reaction Time

Fig. 2 presents the relative contents of various products as a function of reaction time at 265 °C in NCW. Only phenol was detected among the decomposition products. Its relative content increases with longer reaction time.
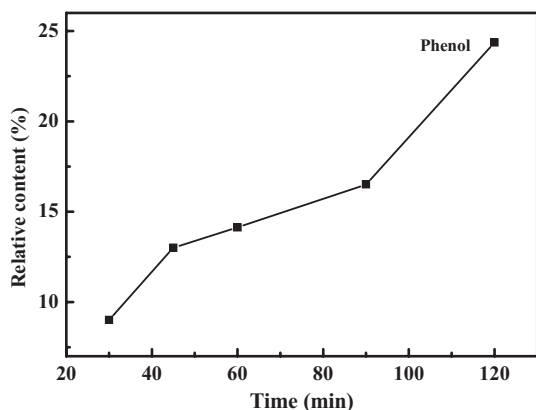
Figure 2. Relative contents of decomposition products of model compound I at different reaction times and 265 °C in NCW.

It is inferred that under the nucleophilic attack of water at a low temperature of 265 °C the terminal ether bond of the model compound undergoes hydrolysis, giving rise to phenol [33] which happens more readily than at the middle ether bond due to higher positive electron density at the terminal ether bond. Fig. 3 illustrates the proposed decomposition mechanism at 265 °C in NCW.

The chemical structure of the decomposition products at 285 °C is given in Fig. 4. Besides phenol, bisphenol-A and 1,2-propanediol-3-phenoxy were also detected. The relative content of various products as a function of reaction time at 285 °C is displayed in Fig. 5. The relative content of all decomposition products increases with longer reaction time. A significant increase of the relative content of phenol could be ob-
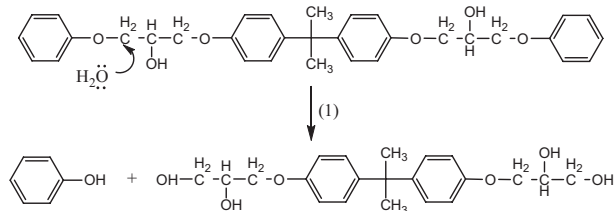
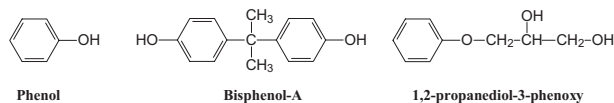**Figure 3.** Decomposition mechanism of model compound I at 265 °C in NCW.

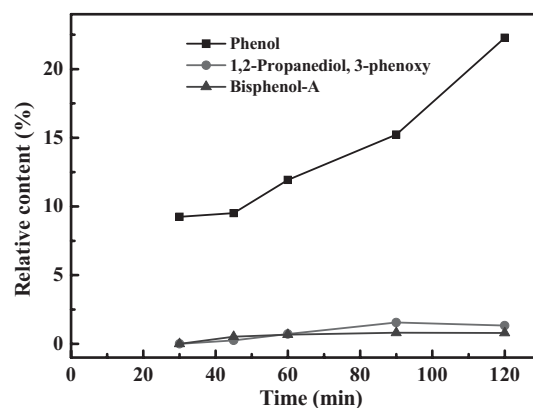**Figure 4.** Chemical structure of decomposition products of model compound I at 285 °C in NCW.

Figure 5. Relative contents of decomposition products of model compound I at different reaction times and 285 °C in NCW.

served, indicating the high impact of the reaction time on the cleavage of the terminal ether bond at higher temperatures.

Given the decomposition products obtained at 285 °C in NCW, both the end and middle ether bonds are assumed to be hydrolyzed when the temperature is increased to 285 °C. However, the terminal ether bond can be broken down more easily than the middle ether bond, which is confirmed by the higher relative content of phenol compared to that of 1,2-propanediol-3-phenoxy. The proposed decomposition mechanism is indicated in Fig. 6.
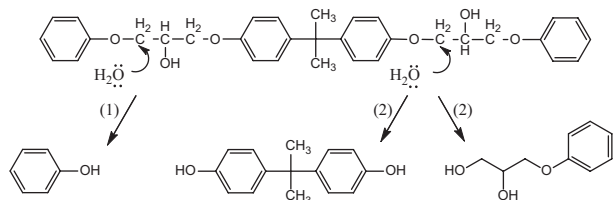
Figure 6. Proposed decomposition mechanism of model compound I in NCW at 285 °C.

3.3 Decomposition Products of Epoxy Model Compound II in NCW at Different Temperatures and Reaction Time

Fig. 7 indicates the relative content of various decomposition products as a function of reaction time in NCW at 285 °C. Within a short reaction time of 30 or 60 min, phenol, benzofuran-2-methyl, 2-propanone-1-phenoxy, 1,2-propanediol-3-phenoxy, and 2-propanol-1,3-diphenoxy were detected among the decomposition products. Upon further increasing the reaction time to > 90 min, another product, piperazine-1,4-dimethyl, can also be identified.
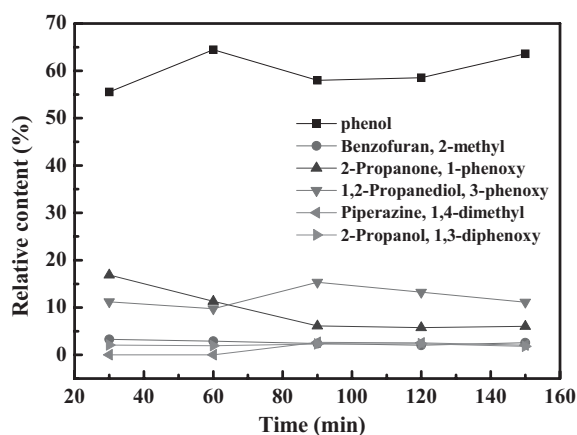

Figure 7. Relative contents of decomposition products of compound II at different reaction times in NCW at 285 °C.

The chemical structures of all decomposition products are presented in Fig. 8. The decomposition mechanism of model compound II at 285 °C in NCW is illustrated in Fig. 9. Under catalysis of H⁺ or water, both the tertiary amine bond and ether bond are hydrolyzed, giving rise to phenol, 1,2-propanediol-3-phenoxy, and N,N'-dimethyl-1,2-ethanediamine (NND), respectively. As a gas product, NND was not detected in the liquid phase. With longer reaction time, more NND was produced, and two NND molecules formed piperazine-1,4-dimethyl by intramolecular cyclization. 1,2-Propanediol-3-phenoxy and phenol also further reacted leading to 2-propanol-1,3-diphenoxy. In NCW, under the electrophilic attack of

proton H⁺ on the hydroxide group of 1,2-propanediol-3-phenoxy, an unstable carbon cation intermediate could be formed by releasing a water molecule. Resonance stabilization of the cation, i.e., delocalization of electrons, followed by loss of a proton, gave rise to 2-propanone-1-phenoxy. Benzofuran-2-methyl can also be formed in the same manner, as depicted in Fig. 9.

Phenol and 1,2-propanediol-3-phenoxy are in negative correlation because the tertiary amine bond and the ether bond cannot break at the same time, and therefore, the increase of the relative content of phenol would lead to a reduced relative content of 1,2-propanediol-3-phenoxy, and vice versa. The relative content of phenol does not increase significantly with longer reaction time (Fig. 7). The reasons for this phenomenon might be that most of the phenol generated from the decomposition of the model compound was consumed by reacting with 1,2-propanediol-3-phenoxy, thus the increase of the relative content of phenol appears not remarkable. A similar situation is observed for 1,2-propanediol-3-phenoxy. The relative content of piperazine-1,4-dimethyl increased with longer reaction time and finally levels off.

Fig. 10 indicates the relative content of various products as a function of reaction time at 305 °C in NCW. The same decomposition products are detected with the products exhibiting similar trends to those at 285 °C, thus it can be concluded that a similar decomposition mechanism occurs (Fig. 9).

The relative content of various products as a function of reaction time at 325 °C is presented in Fig. 11. The trends of the products differ from those at 305 °C and 285 °C. The relative content of phenol decreases with longer reaction time in contrast to 1,2-propanediol-3-phenoxy. Interestingly, phenol remains the dominant decomposition product. The phenomenon can be explained by the fact that at relatively lower temperatures of 285 °C or 305 °C, water acts as the main nucleophilic reactant. The ether bond is broken down more easily than the tertiary amine bond during catalysis of water, therefore, more phenol than 1,2-propanediol-3-phenoxy is produced. When the temperature is increased to 325 °C, the cleavage of the tertiary amine bond is favored compared to the ether bond, for which less activation energy is required. However, the ether bond can still be broken down more readily under the catalysis of higher concentrated H⁺ dissociated by water at higher temperatures. Therefore, the relative content of phenol will be higher than that of 1,2-propanediol-3-phenoxy.
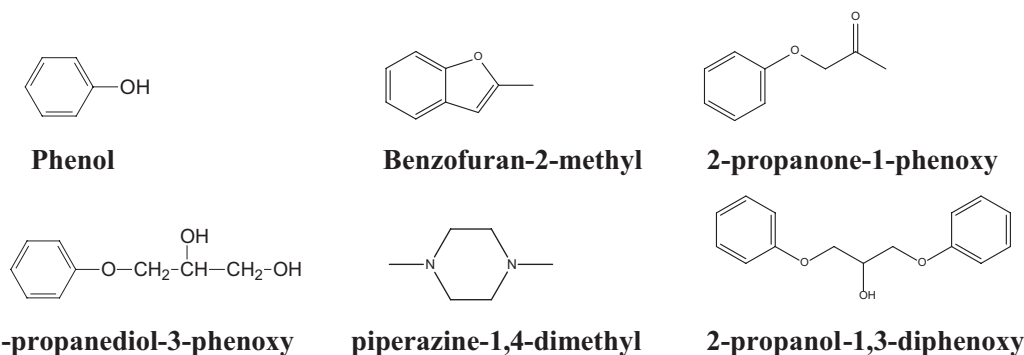

| Phenol | Benzofuran-2-methyl | 2-propanone-1-phenoxy |
| 1,2-propanediol-3-phenoxy | piperazine-1,4-dimethyl | 2-propanol-1,3-diphenoxy |

Figure 8. Chemical structures of decomposition products of model compound II at 285 °C in NCW.
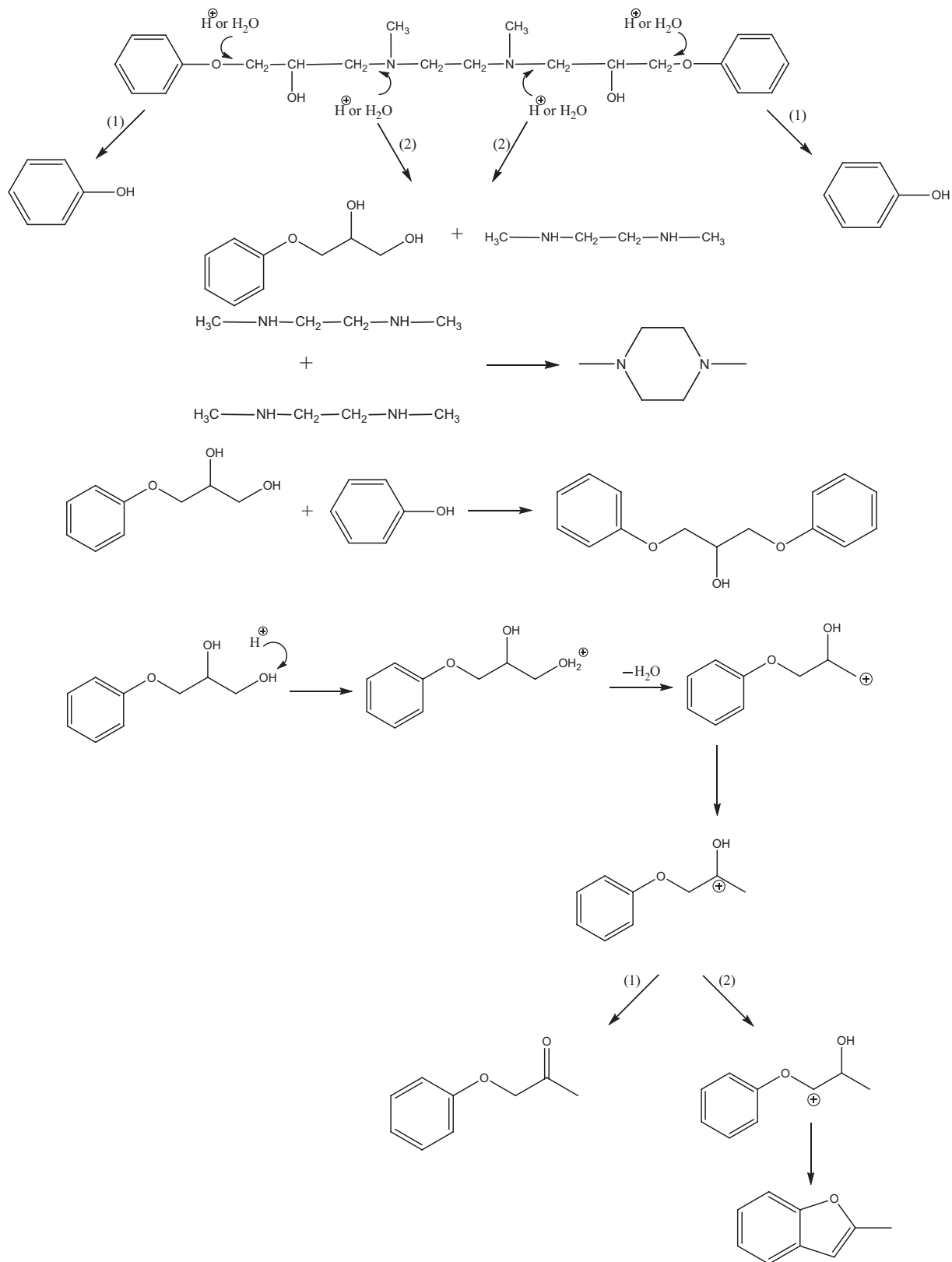
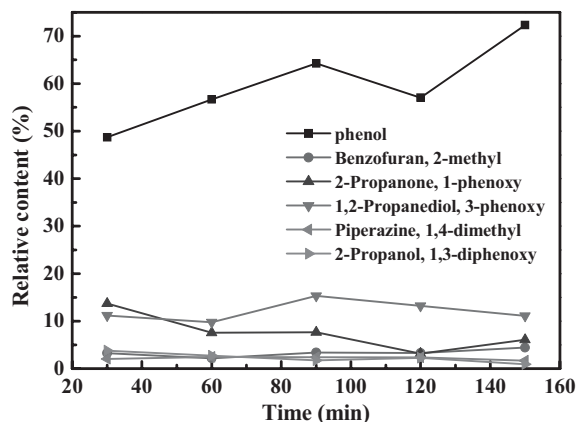**Figure 9.** Decomposition mechanism of model compound II at 285 °C in NCW.

Figure 10. Relative content of decomposition products at different reaction times and 305 °C in NCW.
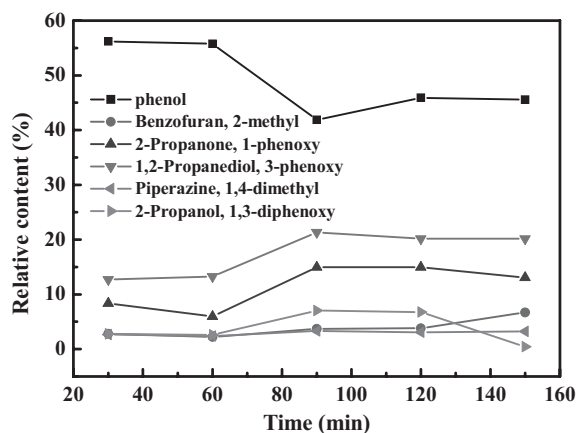

Figure 11. Relative contents of decomposition products at different reaction times and 325 °C in NCW.

Considering the GC-MS results, there is no change in the decomposition products resulting from 285 °C, 305 °C, and 325 °C. Consequently, it can be assumed that raising the temperature will not change the cleavage way of the bonds, but only leads to more complicated reactions among the decomposition products.

4   Conclusions

Two types of epoxy resin model compounds were prepared. The results of FTIR, ^{1}H NMR, and MS confirmed the chemical structure of the compounds synthesized. Both model compounds were decomposed in NCW under different experimental conditions. For model compound I, containing an ether bond and bisphenol-A structure, the terminal ether bond is broken down as a result of the attack of water molecules at 265 °C, giving rise to the product phenol. When the temperature was increased to 285 °C, the middle ether bond in the model compound began to be cleaved, yielding bisphenol-A

and 1,2-propanediol-3-phenoxy. For model compound II, both the tertiary amine bond and ether bonds can be broken down at 285 °C, 305 °C, and 325 °C. The latter happens more readily because of catalysis of H$^+$ in the NCW.

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