

Yuyan Liu¹
Huige Wei¹
Songquan Wu¹
Zhanhu Guo²

Research Article

Kinetic Study of Epoxy Resin Decomposition in Near-Critical Water

¹ Harbin Institute of Technology, Department of Chemical Engineering and Technology, Harbin, China.

² Lamar University, Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Beaumont, TX, USA.

A diglycidyl ether type epoxy resin from bisphenol A, E-51, was cured by methylhexahydrophthalic anhydride (MeHHPA) and then decomposed in near-critical water without any additives. The effects of the experimental parameters such as the reaction temperature, reaction time, pressure, and feedstock ratio on the percentage of decomposition were investigated to obtain optimized reaction conditions. The results revealed that the percentage of decomposition can be enhanced by increasing either temperature or reaction time. At 260 °C, it initially increased with higher pressure and then decreased dramatically when the pressure further was reduced to the saturated water vapor pressure. The kinetics study of the epoxy decomposition was also carried out by monitoring the glass transition temperature of the solid product using differential scanning calorimetry. The decomposition equation was established and the activation energy was calculated to be 123.5 kJ mol⁻¹.

Keywords: Epoxy decomposition, Kinetics, Near-critical water

Received: September 15, 2011; *revised:* October 14, 2011; *accepted:* November 23, 2011

DOI: 10.1002/ceat.201100494

1 Introduction

Increasing production and applications of epoxies [1] and their composites [2–4] have attracted attention to the recycling of these epoxy wastes which are difficult to dispose owing to their cross-linked structures. Several technologies have been developed to dispose epoxy and other polymer wastes [5]. For example, relatively inexpensive and simple mechanical treatment by crushing and milling provides short fibers with poor mechanical properties which can be used as filler or reinforcement materials [6, 7]. Pyrolysis allows for the recovery of long fibers, however, shortcomings are reduced mechanical properties and oxidation of the polymers [8, 9].

Chemical recycling is emerging as a promising approach to convert epoxy wastes to their monomers or petrochemical feedstock which has attracted much interest in recent years [10–12]. 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. Solvolytic processes such as methanolysis, glycolysis, hydrogenolysis, and alcoholysis [13–16] have been reported to decompose epoxy resin into its original mono-

mers. However, the potential toxicity of solvents and high-cost separation of the solvents from the chemical feedstock are severe problems.

Supercritical water (SCW), i.e., water above its critical point ($T_c = 373.946$ °C, $P_c = 22.064$ MPa) and near-critical water (NCW), i.e., water at 250–300 °C, turn out to be alternative candidates due to the fact that water is safe, nontoxic, 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 [17–20], though some water-soluble organics like phenolic compounds and acids were also observed [21].

SCW and NCW as media for biomass processing and chemical synthesis in the presence of acid or base catalysts or transition metal salts have been reported [22–26]. 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, could be readily decomposed into their monomers by hydrolysis in SCW or NCW [27–30]. Other polymers such as phenol resin, however, are relatively difficult to be decomposed, and proper agents are needed to accelerate decomposition [31].

Compared to SCW, NCW requires lower temperature and thus reduces the subsequent operation cost, while maintaining a high ion constant (K_w ; $K_w = [H^+][OH^-]$) and low dielectric constant to serve as a suitable solvent and reaction medium for disposing epoxy wastes. So far, the decomposition of epoxy

Correspondence: Y. Y. Liu (liuyy@hit.edu.cn), Harbin Institute of Technology, Department of Chemical Engineering and Technology, Harbin 150001, China.

in NCW without agents has rarely been reported yet. Here, the decomposition of a model epoxy is investigated in NCW over a temperature range of 260–300 °C without any additives. Parameters including reaction temperature, reaction time, feedstock ratio, and pressure are examined to obtain the optimized reaction environment. The decomposition kinetics are studied and discussed as well.

2 Experimental

2.1 Materials

A diglycidyl ether type epoxy resin from bisphenol A with an epoxy value of 0.48–0.54 mol, E-51, was purchased from LanXing Chemical Co. (China). The curing agent, methylhexahydrophthalic anhydride (MeHHPA), was provided by Wuxi Huili Synthesized Materials Co. (China) and glycidyl phenyl ether by Tokyo Chemical Industry Co. (Japan). The chemical structures of these compounds are illustrated in Fig. 1.

2.2 Preparation of Epoxy Specimens

MeHHPA was added into E-51 at a ratio of MeHHPA:E-51 = 75.2:100 (wt/wt) and stirred constantly with a glass rod until the resin and the curing agent were mixed well. Then, the homogeneous mixture was cured in an aluminum mold according to the recommended curing procedures by the company: 80 °C for 2 h and 160 °C for another 6 h. Finally, the transparent colorless epoxy was cut into identical epoxy specimens of 20 mm × 20 mm × 20 mm.

2.3 Decomposition of Epoxy Specimens

Epoxy specimens were decomposed in a stainless-steel batch reactor (5 cm inner diameter, 20 cm length) with a volume of 100 mL, which consists of a body and a fastening cap. An

epoxy specimen was weighed, put into the reactor, and distilled water according to the feedstock ratio (weight of the epoxy specimen to volume of distilled water) was added. Then the reactor was sealed, heated in an electric furnace for a certain time, and cooled to ambient temperature in a cold-water bath. Then the solid residues, if any in the reactor, were removed, immersed in acetone for 24 h, washed with distilled water, and dried in a vacuum oven. Finally, the solid products obtained were weighed to calculate the percentage of decomposition (d_p) according to Eq. (1). The corresponding acetone was collected to identify the liquid products by high-performance liquid chromatography (HPLC).

$$d_p = (W_0 - W_t)/W_0 \times 100\% \quad (1)$$

where W_0 is the weight of the pristine epoxy resin specimen and W_t is the weight of the solid products. The experiment was repeated following the same procedure to obtain the percentage of decompositions under different experimental conditions.

2.4 Kinetic Study of the E-51/MeHHPA System Decomposition

More than twenty kinds of compounds were identified by HPLC in the acetone solvents obtained from different reaction conditions. T_g of the solid products was applied to simplify the kinetic study of the decomposition reaction [32–34]. The cleavage of the cross-linked bondings was assumed to be a first-order reaction, in which H^+ and OH^- present in NCW were expected to serve as catalysts; see Eq. (2).

$$\frac{dC}{dt} = -kC \quad (2)$$

where C is the concentration of the cross-linked bondings remaining in the epoxy and k is the rate constant. It was

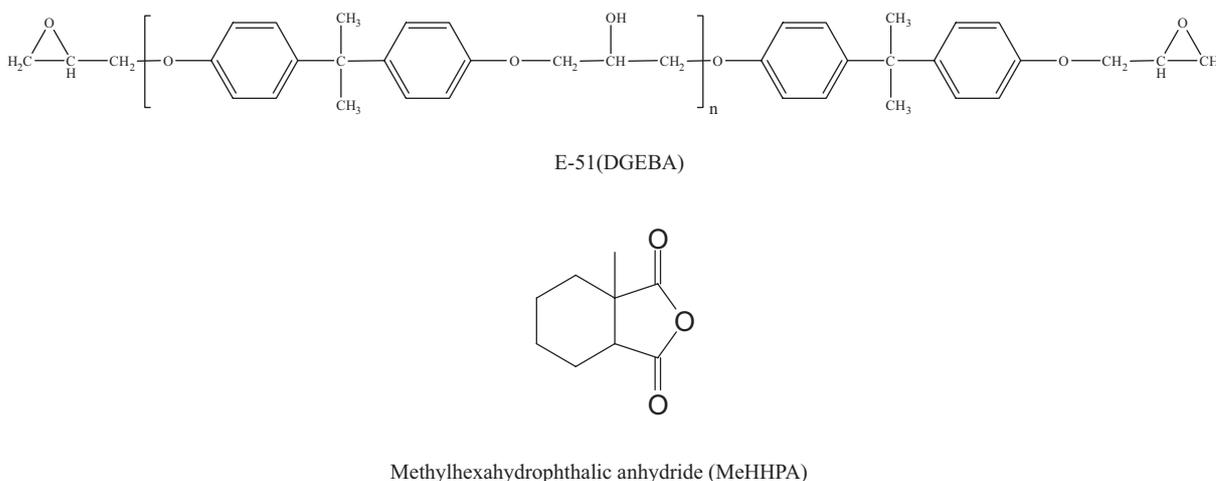


Figure 1. Chemical structures of epoxy resin E-51 and the curing agent MeHHPA.

assumed that T_g of the solid products was proportional to the concentration of the remaining cross-linked bondings [32]. Therefore, T_g is linearly changed with respect to the reaction time according to Eq. (3):

$$T_g = A^{(-kt)+B} \quad (3)$$

where A is the pre-exponential factor and B is the reaction constant. Utilizing T_g values of the solid products at different reaction times at a certain temperature provides the rate constant, k , at that temperature. Rate constants could be obtained in the same way. A differential scanning calorimeter (TA Instruments Q200) was employed to obtain T_g of the solid products.

According to the Arrhenius equation it follows:

$$\ln k = \ln F - E_a/RT \quad (4)$$

where E_a is the activation energy, R is the universal gas constant, and F is the pre-exponential factor. The activation energy can be achieved using the rate constants at different temperatures.

3 Results and Discussion

3.1 Effects of Experimental Parameters on the Percentage of Decomposition

3.1.1 Effect of Reaction Time

The effect of reaction time on the percentage of decomposition of the E-51/MeHHPA system was studied at 260 °C, with a feedstock ratio of 1 g:5 mL and a pressure of 3.0 MPa. Fig. 2 presents the percentage of decomposition as a function of reaction time. After 15 min, the solid residues turned from transparency to translucency and cracks were observed on the residue surface while water and acetone were still clear and colorless. The percentage of decomposition was calculated to be less than 1.6 %, indicating that the mass transfer predominated over the course, with distilled water diffusing into the epoxy resin, and little external decomposition reaction happened. Thirty minutes later, the percentage of decomposition increased to 10.5 %. The shape of the solid residues was observed to be changed. The surface became much tougher with more cracks. Accordingly, water became opaque and the acetone solvent turned to be slightly yellow. These phenomena combined with the higher percentage of decomposition indicated that internal decomposition occurred, and the cross-linked structure was partly destroyed during this process.

As the reaction proceeded from 30 to 60 min, i.e., the main decomposition stage, the epoxy resin began to be decomposed at a larger scale, with 59.6 % at 30 min and 88.2 % at 60 min percentage of decomposition (Fig. 2). The solid residues lost their original shape, with little epoxy resin remaining after being washed by acetone, which turned to be dark-brown. After 75 min, the percentage of decomposition already reached 100 %, and no solid residues remained.

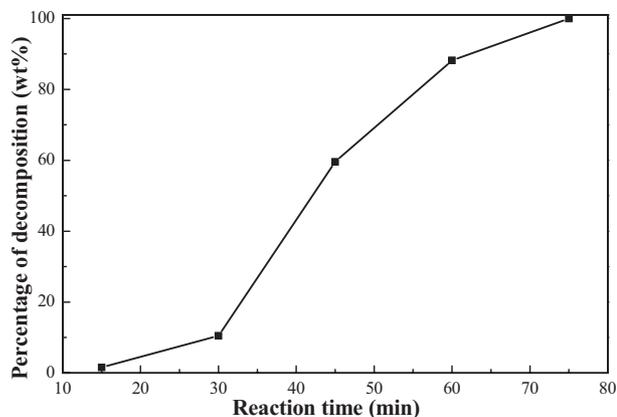


Figure 2. Percentage of decomposition versus reaction time at 260 °C, with a feed ratio of 1 g:5 mL and a pressure of 3.0 MPa.

3.1.2 Effect of Reaction Temperature

The decomposition reactions were conducted at temperatures ranging from 260 °C to 300 °C for 15 min with a feedstock of 1 g:5 mL. Fig. 3 displays the percentage of decomposition as a function of reaction temperature, being 1.6 %, 2.2 %, 9.2 %, 15.9 %, and 33.1 % under temperatures of 260 °C, 270 °C, 280 °C, and 290 °C, respectively. The surface of the solid epoxy resin was observed to become tougher and to have more cracks with increasing the reaction temperature.

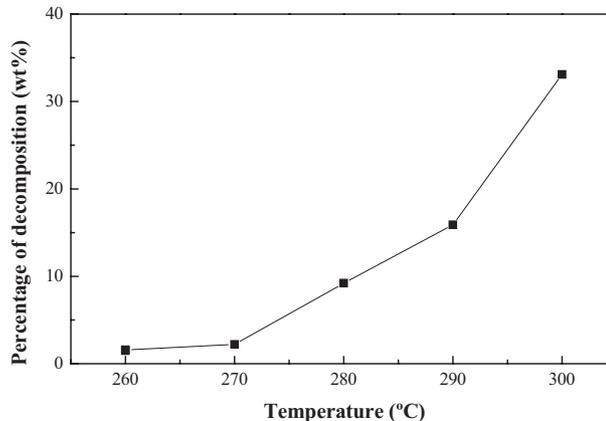


Figure 3. Percentage of decomposition versus temperature after a reaction time of 15 min, with a feedstock of 1 g:5 mL.

Decomposition reactions at 30, 45, 60, 75, and 90 min within this temperature range were also performed. It was discovered that the percentage of decomposition reached 100 % after 30 min at 280 °C, 290 °C, and 300 °C. However, the colors of the corresponding acetone solvents were different, appearing shadow-yellow at 280 °C, brown at 290 °C, and dark-brown at 300 °C. The solid residues also showed different physical properties as a brown sticky solid at 280 °C and dark-brown oil at 300 °C. The components present in the residues were detected by HPLC to be different organic compounds. The results indicated that the temperature had a significant effect on the per-

centage of decomposition and composition of the decomposition products.

3.1.3 Effect of Pressure

The effect of pressure on the epoxy resin percentage of decomposition was studied at 260 °C for 75 min. The pressure can be finely tuned by manipulating the amount of water since the pressure increased with increasing the water volume in the reactor. Fig. 4 indicates the percentage of decomposition as a function of pressure. The pressure had a remarkable effect on the percentage of decomposition which initially increased with increasing the pressure and approached a maximum of 49.3 % at 6.8 MPa, but declined dramatically when the pressure further increased to around 7.0 MPa, a saturated vapor pressure for water at 260 °C. This phenomenon can be explained as follows. On the one hand, the pressure in the reactor increased significantly with increasing the amount of water in the beginning and gave rise to an enhanced ion constant (K_w). On the other hand, most of water was capable of evaporating into a gaseous state before reaching the saturated vapor pressure, facilitating the reaction between water and the resin specimen with high diffusivity and rapid mass transfer. However, when water was further added, the pressure increased slightly and leveled off to 7.0 MPa, having a limited effect on the increase of K_w . In addition, too much water resulted in excessive water remaining in the liquid state, covering the surface of epoxy resin and imposing interphase mass transfer restrictions on water vapor molecules from diffusing into and reacting with resin, thus reducing the reaction rate and lowering the percentage of decomposition.

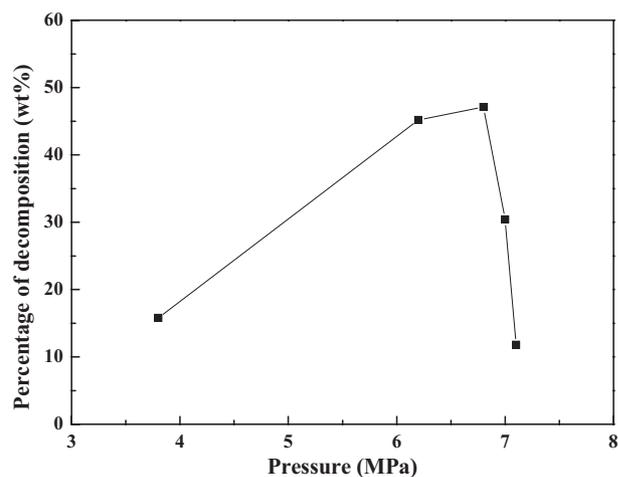


Figure 4. Percentage of decomposition at different pressures at 260 °C after a reaction time of 75 min.

3.1.4 Effect of Feedstock Ratios

The effect of feedstock ratios on the percentage of decomposition was studied at 260 °C for 75 min under a pressure of 6.0 MPa (Fig. 5). The feedstock ratio is observed to have a neg-

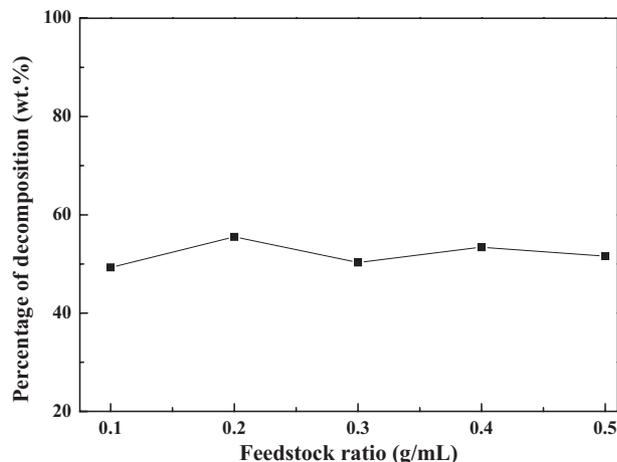


Figure 5. Percentage of decomposition versus the feedstock ratio at 260 °C after a reaction time of 75 min with a pressure of 6.0 MPa.

ligible impact on the percentage of decomposition, with percentages of decomposition of 49.3 %, 55.5 %, 50.3 %, 53.4 %, and 51.6 %, when the feedstock ratio was 1 g:10 mL, 2 g:10 mL, 3 g:10 mL, 4 g:10 mL, and 5 g:10 mL, respectively. The minor difference can be explained by the fact that at the same temperature, pressure became the primary factor in determining the percentage of decomposition. With the same amount of water, the pressure was about the same for all reaction systems, so the percentage of decompositions differed only slightly.

3.2 Kinetic Study of Epoxy Resin Decomposition

T_g of the solid product for different reaction times and temperatures was obtained using differential scanning calorimetry (DSC). DSC spectra of the solid product at different reaction times at 230 °C are displayed in Fig. 6, where (a) stands for a reaction time of 15 min, (b) for 30 min, (c) for 45 min, and (d) for 60 min; T_g was 54.33 °C, 46.75 °C, 46.56 °C, 44.78 °C, and 40.6 °C, respectively. T_g at the other temperatures was achieved in the same way. It turned out that T_g decreased with increasing the reaction time, which was consistent with the increased degree of destroyed cross-linked structure in the epoxy system over the course. Employing the data of T_g and reaction time provided exponential curves at different temperatures in Fig. 7, with (a) 220 °C, (b) 230 °C, (c) 240 °C, and (d) 250 °C, respectively. The exponential curves at 220 °C, 230 °C, 240 °C, and 250 °C gave $\ln k$ of -3.5763 , -3.0025 , -2.7673 , and -1.7312 , respectively. The coefficients of these reaction rates were calculated and are summarized in Tab. 1. Fig. 8 presents the plot of $\ln k$ versus $1/T$ from the slope of which the activation energy was calculated to be $123.5 \text{ kJ mol}^{-1}$ according to Eq. (4), which is a quite reasonable value for epoxy decomposition reaction [7, 26].

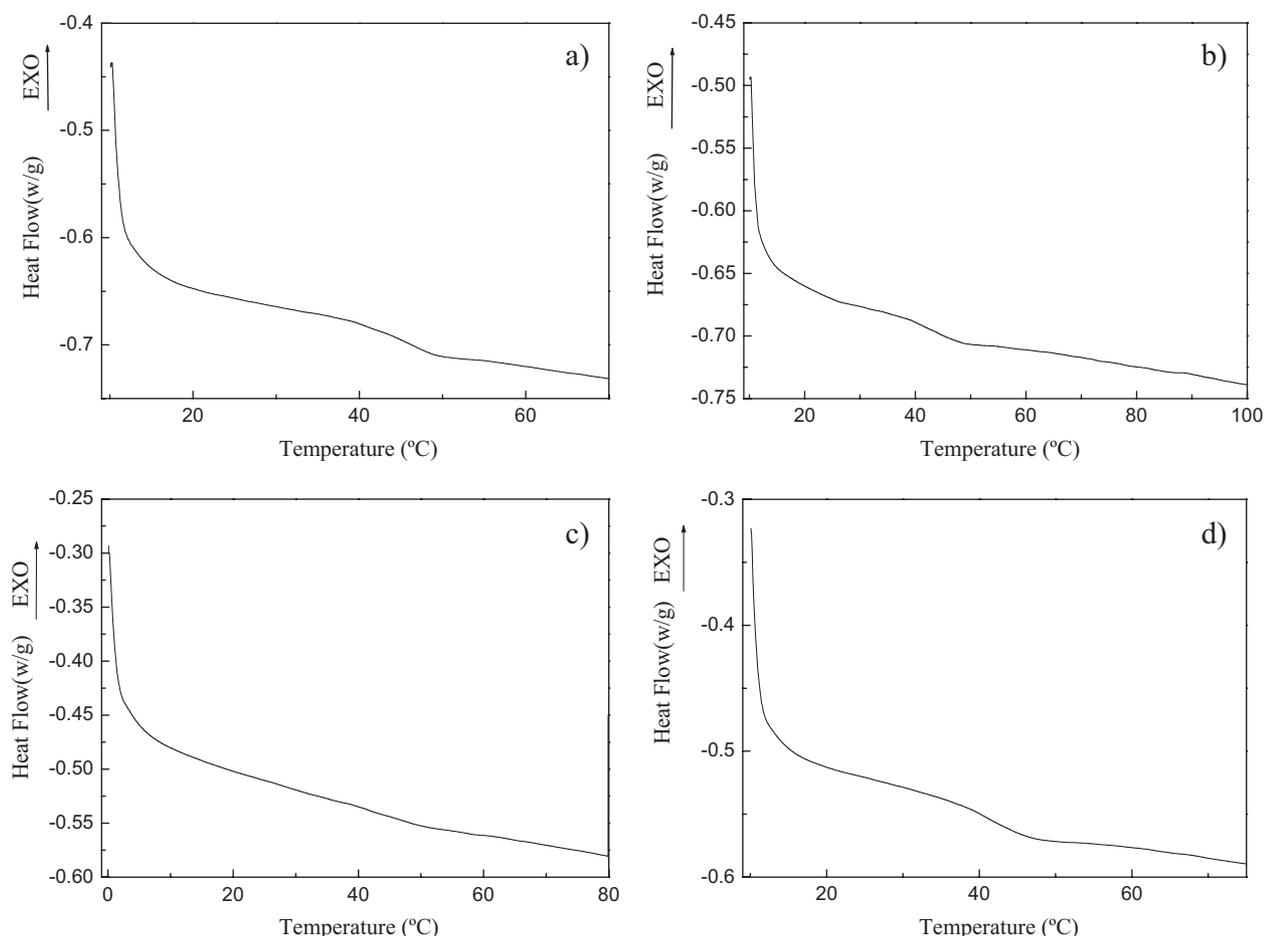


Figure 6. DSC spectra of the solid products obtained after the reaction at 230 °C for (a) 15; (b) 30; c) (45; and (d) 60 min, respectively.

Table 1. Coefficients of reaction rate at different temperatures.

T	220 °C	230 °C	240 °C	250 °C
k [min ⁻¹]	0.027978	0.049662	0.051757	0.177069

4 Conclusions

Epoxy resin was demonstrated to be successfully decomposed in near-critical water in the absence of any additives. The decomposition reaction began with the surface reaction, and then the cross-linked structure started to be destroyed and was further decomposed into small molecules. The temperature affected the epoxy decomposition by increasing the percentage of decomposition and changing the decomposition products. High percentage of decomposition was controlled by deliberately tuning the pressure by adjusting the amount of water at comparatively low temperature, which has potential to reduce the operating cost. The feedstock ratio contributed little to the percentage of decomposition when the reaction temperature

and pressure remained constant. The kinetic study indicated that the activation energy for the cured epoxy resin decomposition was 123.5 KJ/mol.

Acknowledgment

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China under Project No. 50973023, Z. Guo from the National Science Foundation USA under Grant No. CBET 11-37441. We also express our gratitude to Guohua Shan for his partial contribution to this work.

The authors have declared no conflict of interest.

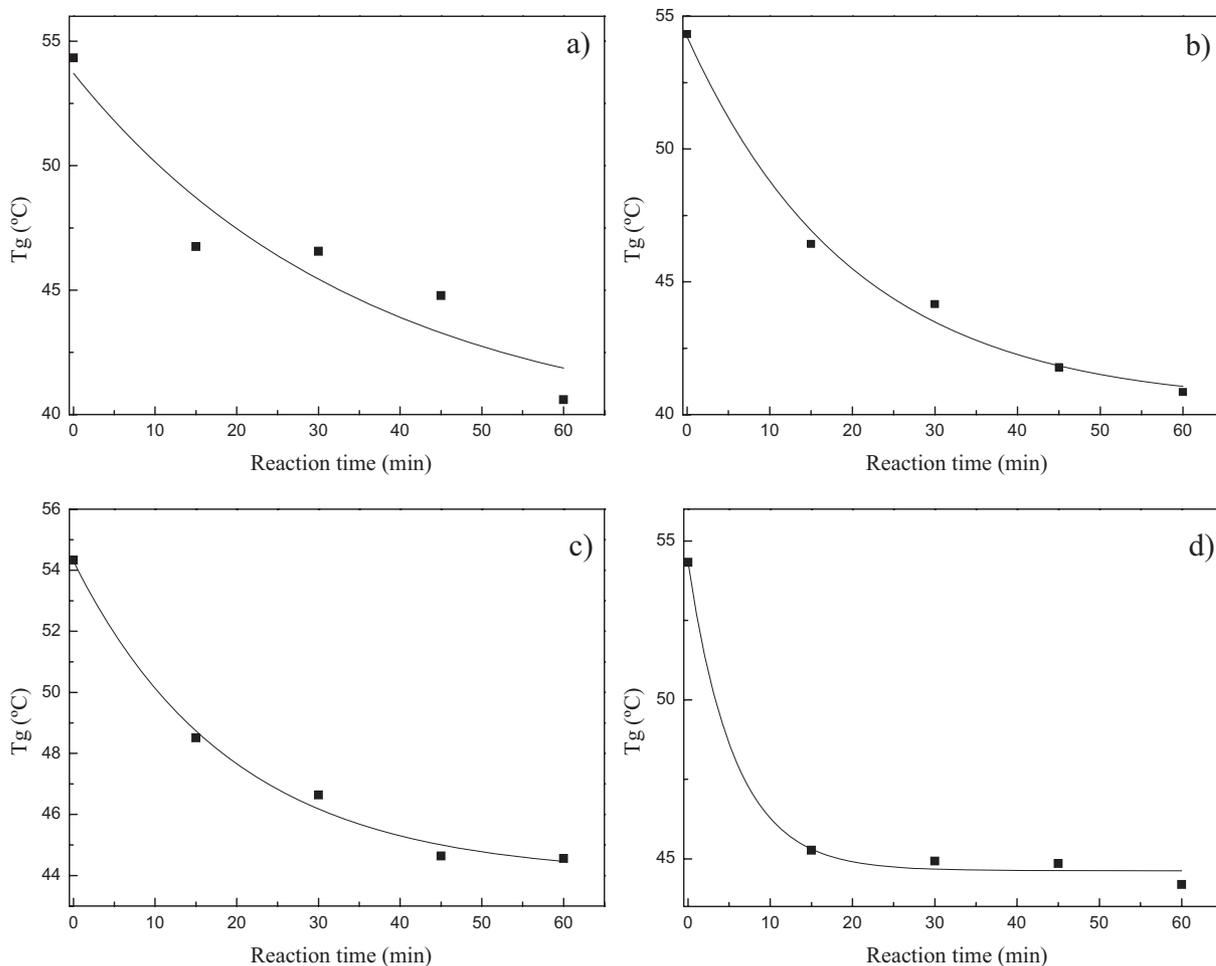


Figure 7. T_g versus reaction time of the solid residues obtained at temperatures of (a) 220 °C, (b) 230 °C, (c) 240 °C, and (d) 250 °C, respectively.

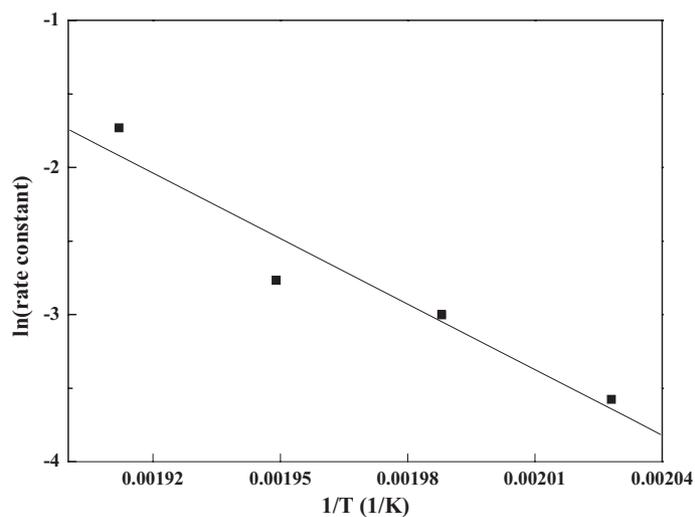


Figure 8. $\ln k$ (rate constant) versus $1/T$.

References

- [1] Z. Wang, X. Yang, Q. Wang, H. T. Hahn, S. Lee, K. H. Lee, Z. Guo, *Int. J. Smart Nano Mater.* **2011**, *2*, 176.
- [2] J. Zhu, S. Wei, A. Yadav, Z. Guo, *Polymer* **2010**, *51*, 2643.
- [3] J. Zhu, S. Wei, J. Ryu, M. Budhathoki, G. Liang, Z. Guo, *J. Mater. Chem.* **2010**, *20*, 4937.
- [4] J. Zhu, S. Wei, J. Ryu, L. Sun, Z. Luo, Z. Guo, *ACS Appl. Mater. Interfaces* **2010**, *2*, 2100.
- [5] J. Zhu, S. Wei, Y. Li, S. Pallavkar, H. Lin, N. Haldolaarachchige, Z. Luo, D. P. Young, Z. Guo, *J. Mater. Chem.* **2011**, *21*, 16239.
- [6] K. Ogi, T. Shinoda, M. Mizui, *Composites, Part A* **2005**, *36*, 893.
- [7] C. Gallet, M. Kermarrec, *JEC Composites* **2006**, 71.
- [8] R. E. Allred, A. B. Coons, R. J. Simonson, *Proc. Technol. Trans. Global Community*, ProQuest, Ann Arbor **1996**, 139.

- [9] H. Yip, S. Pickering, C. Rudd, *Plast., Rubber Compos. Process. Appl.* **2002**, 31, 278.
- [10] T. Yoshioka, T. Sato, A. Okuwaki, *J. Appl. Sci.* **1994**, 52, 1353.
- [11] Z. Zhang, T. Hirose, S. Nishio, Y. Morioka, N. Azuma, A. Ueno, *Ind. Eng. Chem. Res.* **1995**, 34, 4514.
- [12] J. Chen, C. Ober, M. Poliks, *Polymer* **2002**, 43, 131.
- [13] T. Sako, T. Sugeta, K. Otake, N. Nakazawa, M. Sato, K. Nami-ki, M. Tsugumi, *J. Chem. Eng. Jpn.* **1997**, 30, 342.
- [14] K. E. Gersifi, G. Durand, G. Tersac, *Polym. Degrad. Stab.* **2006**, 91, 690.
- [15] D. Braun, W. Von Gentzkow, A. Rudolf, *Polym. Degrad. Stab.* **2001**, 74, 25.
- [16] R. Pinero-Hernanz, J. Garcia-Serna, C. Dodds, J. Hyde, M. Poliakoff, M. J. Cocero, S. Kingman, S. Pickering, E. Lester, *J. Supercrit. Fluids* **2008**, 46, 83.
- [17] P. E. Savage, *J. Supercrit. Fluids* **2009**, 47, 407.
- [18] A. Kruse, H. Vogel, *Chem. Eng. Technol.* **2008**, 31, 1241.
- [19] A. Kruse, E. Dinjus, *J. Supercrit. Fluids* **2007**, 39, 362.
- [20] M. Goto, *J. Supercrit. Fluids* **2009**, 47, 500.
- [21] C. Fromonteil et al., *Ind. Eng. Chem. Res.* **2000**, 39 (4), 922.
- [22] Y. T. Matsumura, S. R. Minowa, B. Potic, A. Kersten, W. Prins, W. P. M. van Swaaij, B. van de Beld, D. C. Elliott, G. G. Neuenschwander, A. Kruse, M. J. Antal Jr, *Biomass Bioenergy* **2005**, 29, 269.
- [23] Y. Matsumura, M. Sasaki, K. Okuda, S. Takami, S. Ohara, M. Umetsu, T. Adschiri, *Combust. Sci. Technol.* **2006**, 178, 509.
- [24] E. Dinjus, A. Kruse, in *High-Pressure Chemistry: Synthetic, Mechanistic, and Supercritical Applications* (Eds: R. van Eldik, F.-G. Klärner), Wiley-VCH, Weinheim **2002**, 422.
- [25] Y. Matsumura, *Biomass Bioenergy* **2005**, 29, 269.
- [26] T. B. Brill, *J. Phys. Chem. A* **2000**, 104, 4343.
- [27] Y. Nagase, M. Yamagata, T. Matsuda, K. Naito, R. Kodama, in *Proc. 5th Meeting on Supercritical Fluids* (Eds: F. Jin, Q. Zhou, B. Wu), American Institute of Physics, Melville **1998**, 127.
- [28] Z. Dai, B. Hatano, J. Kadokawa, H. Tagaya, *Polym. Degrad. Stab.* **2002**, 76, 179.
- [29] M. Goto, M. Umeda, A. Kodama, T. Hirose, S. Nagaoka, *Kobunshi Ronbunshu* **2001**, 58, 548.
- [30] A. Ikeda, K. Katoh, H. Tagaya, *J. Mater. Sci.* **2008**, 43, 2437.
- [31] Y. Suzuki, H. Tagaya, T. Asou, J. Kadokawa, K. Chiba, *Ind. Eng. Chem. Res.* **1999**, 38, 1391.
- [32] J. S. Chen, C. K. Ober, M. D. Poliks, Y. Zhang, U. Wiesner, C. Cohen, *Polymer* **2004**, 45, 1939.
- [33] S. Vyazovkin, N. Sbirrazzuoli, *Macromol. Chem. Phys.* **1999**, 200, 2294.
- [34] J. Barton, *Epoxy Resins Composites I* **1985**, 111.