

Low-Temperature Decomposition of Epoxy Resin

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Abstract: We report a new method using a heating medium for the thermal decomposition of epoxy resin (EP) at temperatures ranging from 50 to 200 °C. EP decomposition also occurred below 50 °C during a 6-day period to generate bisphenol A (BPA) at concentrations as high as 5 ppm. When polyethylene glycol was used as a heating medium, we determined the kinetics of the EP decomposition at low temperature. We determined the apparent activation energy of the overall decomposition to be 40.8 kJ/mol and the frequency factor to be 2.3×10^3 by monitoring the rate of BPA formation. Thus, EP is clearly unstable upon the application of heat.

Keywords: epoxy resin, bisphenol A, endocrine disrupting chemical, low-temperature decomposition, plastic, landfill.

Introduction

Plastic is cheaply and is easy to be produced of large quantities, because the stable property is shown at the living environment. Plastic is disposed in landfill as not recycle, since it generates dioxin, etc. by reacting with the chlorine in the incomplete combustion.¹ Wide area is necessary for landfill, and there are the many problems that the hazardous compounds migrate to water and that it contributes to living organisms.²

Cured epoxy resin is a typical heat-resistant engineering plastic produced with bisphenol A (BPA) as a starting material. Epoxy resin is used to prepare electric and electronic equipment and widely used for paints and household goods. Waste plastic constitutes an environmental pollutant itself³ and the more serious problem is certain chemicals derived from plastics which may seep out from waste plastics in landfill. Recent researches demonstrate that plastics disposed in the nature cause the environmental pollution. Especially the pollutants are usually low-molecular-weight compounds such as styrene oligomer,⁴ nonylphenol,⁵ BPA,⁶ and phthalate

esters (PAE).⁷ BPA has been shown to have adverse effect on reproductive and immunologic functions at lower concentrations under ppm in living organisms.⁸⁻¹⁰ We have little knowledge on the kinetics of the low-temperature decomposition of plastic products in a diary use situations and after being disposed.

The present paper demonstrates that at low temperature, the decomposition of uncured epoxy resin (EP) gives rise to BPA, and thus may be presented even in canned food and water discharged from a landfill.

Experimental

Materials. Uncured epoxy resin (average M_n ca. 4,000) was purchased from Aldrich Chemical Company, Inc. This uncured EP contained 200 $\mu\text{g/g}$ 2,2-bis(4-glycidylphenoxy)propane (BADGE) and trace BPA, which was removed at the concentration less than 0.2 $\mu\text{g/g}$ by reprecipitation with tetrahydrofuran and diethyl ether in three times. The heating medium (polyethylene glycol 1,540, PEG, reagent grade) was used without purification (WAKO, Tokyo Japan). The detailed experimental procedures¹¹ and apparatuses were described previously.¹²

For GC/MS column was CP-Sil 8CB (Chrompack, 30-m

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length \times 0.32 mm I.D., 0.25 m film thick) and for GPC column was Polymer Laboratory Inc., two Mixed-E columns (300 \times 7.5 mm) + 50 A-column (300 \times 7.5 mm), column oven 40 °C) were used in this study.

Calibration Curve. Due to a strong adsorption property of BPA, a GC column was washed with acetone before and after quantitative analysis although the trimethylsilylation of BPA is a typical treatment for GC/MS samples. Possible amounts of BPA adsorption were at 0.01 ppm or less in the analysis. In this study, calibration curve was made by internal standard method, in which diphenyl was added at a constant amount and a coefficient of variation of calibration curve was 0.9994.

Results and Discussion

Temperature Effect on EP Decomposition. Average molecular weight of EP was estimated as 4,000, and molecular weight of BPA is 228. One cannot distinguish the low molecular weight products in the large amounts of polymers. We newly constructed the method in order to solve these problems. It is possible of this newly constructed method that there is no elevated temperature process by using PEG as heating medium, in respect of the thermal decomposition of EP and that it does under the softening point and in use of the living life or after being disposed of EP.

The minute quantity under ppm can determine BPA only in the simple treatment of liquid/ liquid distribution by water. Therefore, this study is regarded as the initial stage of EP decomposition well. The details of method was shown in another report.¹² The EP showed the thermal decomposition at 50 °C, and 5 ppm BPA was formed. The result was shown in Figure 1.

It was shown that the decomposition product in this study was simple unlike the result of other EP thermal decomposition at high temperature.^{13,14} In Japan, canned drinks coated with cured epoxy resin keep 60-65 °C, 7~10 days warm in the vending machine and are sold.¹⁵ The canned food is being heat-treated by the necessity for the sterilization at 121 or 175 °C for several minutes.¹⁶ The result showed that the EP receives the thermal decomposition at the life utilization, and formed endocrine disrupting chemical, BPA.

Figure 2 showed the emitted BPA content according to the heating temperature under the fixed time (3 hrs). It was recognized that the decomposition product was only BPA and it was increased for the rise in the reaction temperature recitilinear. Thermally stable plastic cured EP that it does not decompose in 250 °C or less¹⁷ but uncured EP was decomposed even in the low temperature of 50 °C.

BPA Formation with the Reaction Time. Plastics have been considered to be thermally stable, especially at the ordinary temperatures. Waste plastic was disposed in landfill sites, and the elution of biologically-active compounds to the environment could not be expected until the studies

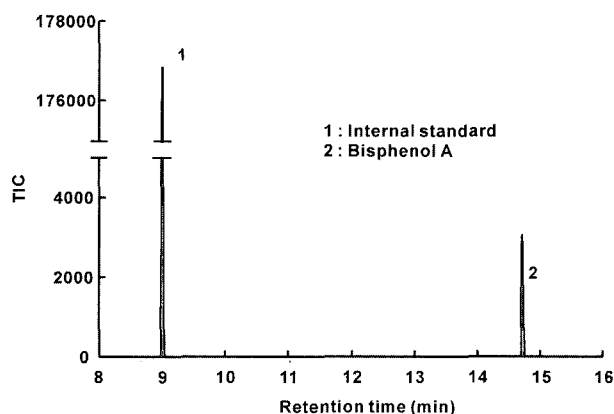


Figure 1. TIC chromatogram of thermal decomposed epoxy resin at 50 °C, 6 days [Selected ion at m/z : 75, 135, 150, 154, 213, 228, 325, 340].

Apparatus: GC/ HP6890. Column, DB-5; 30 m; I.D. 0.32 mm; 0.25 mm. He, 1.5 mL/min. Splitless injection. Injection temperature, 280 °C. Column temperature, 50 °C (2 min hold) to 290 °C (15 °C/min) and 2 min hold. MS/ Jeol JMS-AMII. Interface temperature, 255 °C. Ion source temperature, 210 °C. Electron accelerating voltage, 70 eV.

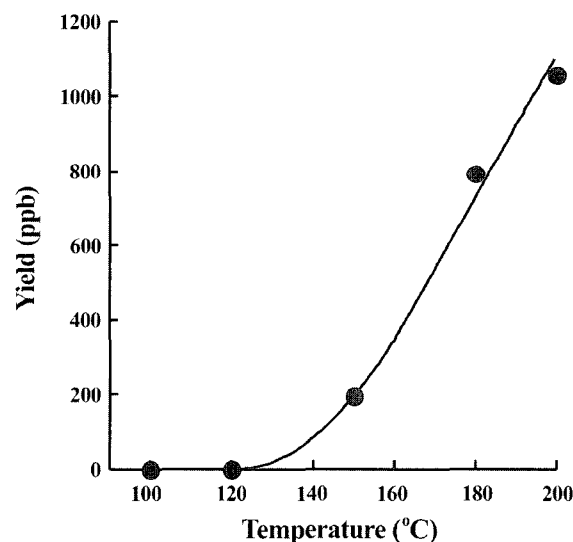


Figure 2. Relationship between the yield of bisphenol A and the temperature on the thermal decomposition of epoxy resin under the fixed time (3 hrs).

on the pollutants like nonylphenol, BPA, and PAE. At the wide temperature range of 50-200 °C, EP was decomposed in PEG. The formation of BPA was monitored with the exposing time. The result was shown in Figure 3.

In Figure 3, the content of emitted BPA was increased with the reaction time at each temperature.

Figure 4 shows the Arrhenius plot of EP decomposition, and the good linearity of the kinetic results was confirmed. The apparent kinetic parameters of the Arrhenius equation were obtained based on the rate constants of BPA formation

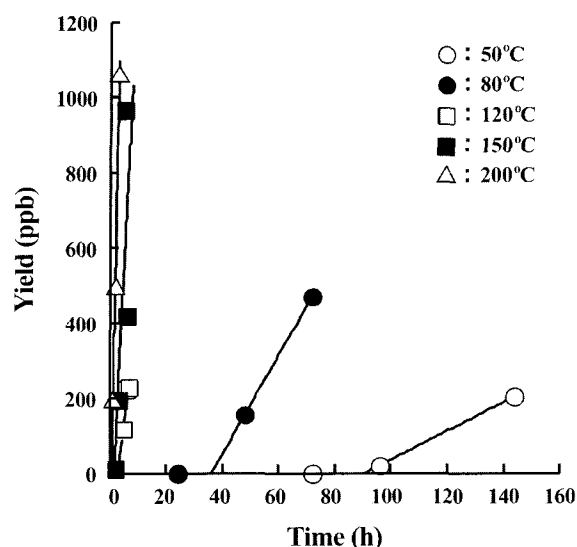


Figure 3. Effect of reaction time on the thermal decomposition of epoxy resin.

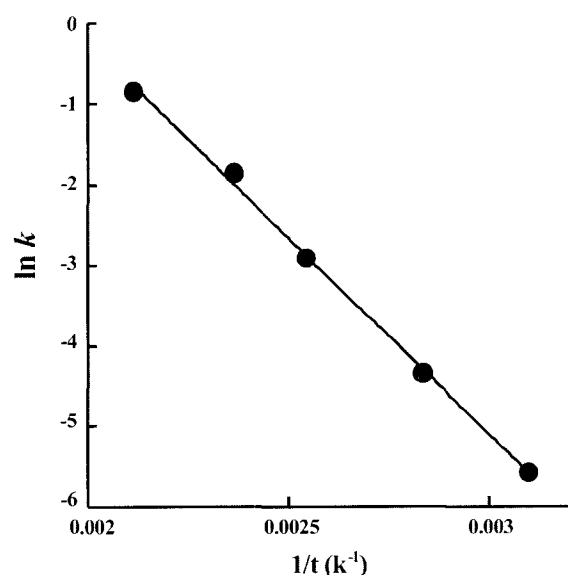


Figure 4. Arrhenius plots of bisphenol A.

at each temperature. The activation energy of the EP decomposition was given as 40.8 kJ/mol and the frequency factor was 2.3×10^3 .

In this study, the uncured EP was powdered in 40-80 mesh, and the resulting sample was dispersed in PEG with stirring (500 rpm). This procedure is the enhanced conditions for the accelerated thermal decomposition. The activation energy of the decomposition was less than that of PAE,¹⁸ thus decomposes more easily than the latter. In the landfills where EP or polycarbonate have been discarded, there is the possibility of long-term pollution by BPA which is generated via the decomposition of those materials since

landfill temperature may remain at 50°C or more for many years.¹⁹

Conclusions

The apparent activation energy of the overall decomposition of EP was calculated as 40.8 kJ/mol, based on the rate of the formation of BPA. In the thermal treatment such as the sterilization of canned food, the similar decomposition of EP may proceed to lead the formation of BPA. There would be several pathways of BPA emission to the environment, and one of the pathway can be a thermal decomposition of BPA-containing plastics like polycarbonate and EP.

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