

# Gamma Radiation Effects on Benzoxazine Monomer: Curing and Thermal Properties

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**Abstract.** Benzoxazine monomer was irradiated with gamma ray at various radiation doses. The curing behaviours of the radiated monomer and thermal stability of the synthesized polymer was observed and compared. The thermograms of differential scanning calorimeter (DSC) reveal that the radiation was able to reduce the energy consumed for polymerization. Furthermore, the peak of polymerization of monomer was lower with increasing the radiation dose. At low radiation dose, the thermograms from thermogravimetric analysis reveal that there was no significant change of degradation temperature and char yield of the synthesized polymer, while the improvement of the degradation temperature and the increase in char yield were observed in the polymer synthesized from benzoxazine monomer radiated at 30 kGy.

**Keywords:** benzoxazine; curing; gamma irradiation.

## 1. Introduction

Polybenzoxazine is a class of thermosetting polymers derived from ring-opening polymerization of their monomers. The polymer possesses various good properties such as near-zero shrinkage upon polymerization as well as high thermal stability and good mechanical properties [1–4], thus this kind of polymer shows high potential in many applications [5–6]. Nowadays, there have been a large number of methods to modify polybenzoxazine for broaden the range of use, such as blending or alloying with other polymers [7-8]. Recently, gamma ray irradiation is extensively investigated as means of modifying properties of polymeric materials, such as films, fibers, powders and molded objects. [9-11] Irradiation with gamma ray was able to induce chemical reactions at any temperature in the solid, liquid and gas phase without need of any catalyst. [12-13] In this study, the polymer was synthesized from the benzoxazine monomer irradiated with gamma ray at various radiation doses. The curing behaviors of the radiated monomer were observed and compared with the pristine polymer.

## 2. Experimental

### 2.1. Materials

Benzoxazine monomer is based on bisphenol-A, aniline, and formaldehyde. Bisphenol-A (commercial grade) was supplied by Thai Polycarbonate Co., Ltd. (TPCC). Paraformaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was obtained from Panreac Quimica SA Company. All chemicals were used without further purification.

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## 2.2. Benzoxazine Monomer Preparation

To synthesize the monomer, bisphenol-A, aniline, and paraformaldehyde were mixed using the patented solventless technology [14]. Normally, the monomer is solid powder at room temperature with yellow color. The powder was ground into fine powder and was kept in a refrigerator for further use without purification.

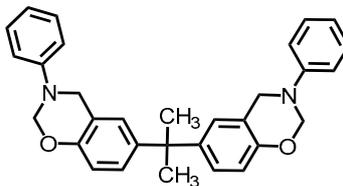


Fig. 1: Synthesized benzoxazine monomer.

## 2.3. Benzoxazine Monomer Preparation

The polymer was obtained from polymerization by heating benzoxazine monomer, which was irradiated at various radiation doses (0, 50, 100, 200 kGy) with dose rate of 8kGy/hour. The heating program of polymerization was 150°C, 200°C, and 240°C (2 hours for each temperature).

## 2.4. Sample Characterization

### 2.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) spectra of the monomer radiated at 0, 10, 50, 100, and 300 kGy were acquired by using a Spectrum GX FT-IR spectrometer from Perkin Elmer. All spectra were taken with 64 scans at a resolution of 4 cm<sup>-1</sup>

### 2.4.2 Differential Scanning Calorimetry (DSC)

Curing temperatures of the polymer synthesized from monomer radiated at 0, 50, 100, and 300 kGy were examined using a differential scanning calorimeter (Mettler Toledo, DSC822e). A 10 mg sample placed in a 50 µL aluminum pans was characterized at 10°C /min from 30-300°C under nitrogen flux (50ml/min).

### 2.4.3 Thermogravimetric Analysis (TGA)

The decomposition temperature (Td) and char yield of the polymer synthesized from monomer radiated at 0, 10, 30, 100 and 300 kGy were studied using TGA Instruments (Mettler Toledo, TGA/SDTA 851e). The samples of approximately 10 mg were heated with the heating rate of 10 °C /min from 40 to 800 °C under nitrogen atmosphere. The flow of nitrogen was kept at 80 ml/min.

## 3. Results and Discussion

### 3.1. Change in Chemical Structure of Monomer

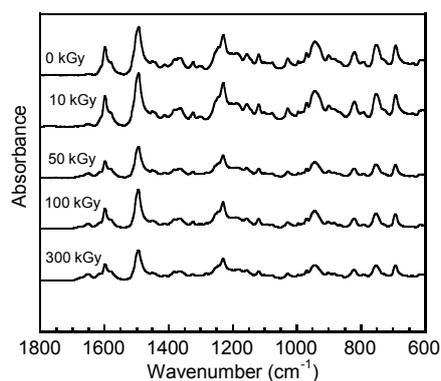


Fig. 2: FT-IR spectra of benzoxazine monomer radiated with various radiation doses.

From the FT-IR spectra in Fig. 2, it could be noticed that the chemical structure of benzoxazine monomer was changed with radiation dose. The height of the spectra, relating with the intensity of the chemical functional group, was found to be changed. The spectra at the wavenumber in the range of 690-900 cm<sup>-1</sup> (aromatic ring), 1323 cm<sup>-1</sup> (C-O stretching), and 1350-1000 cm<sup>-1</sup> (C-N stretching) were reduced especially in high radiation doses. It could be assumed that some chemical chains in benzene ring were possibly broken.

### 3.2 Change in Chemical Structure of Monomer

The curing behaviors of the radiated monomer were determined using DSC thermograms as shown in Fig. 3. The energy consumption for curing of the radiated benzoxazine monomer and the temperature at curing peak were summarized in Table 1. It could be noticed that the temperature of curing peak and heat of curing were decreased with the increase of radiation dose. Fig. 2 and Table 1 could present the advantage of the gamma radiation for lowering the curing temperature of the monomer.

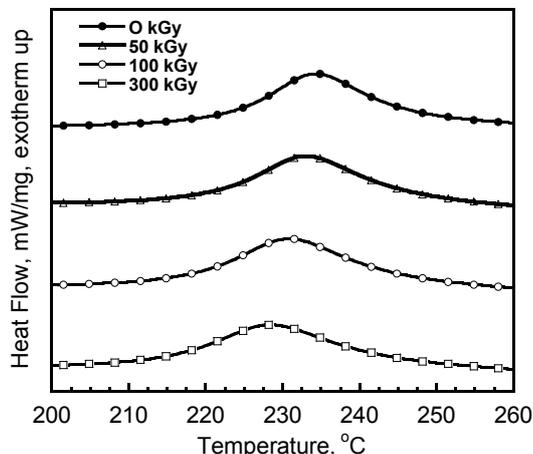


Fig. 3: DSC thermograms of benzoxazine monomer radiated with various radiation doses.

Table 1: Heat of curing and curing peak temperature of benzoxazine monomer radiated at various doses.

Radiation Dose (kGy)	Heat of Curing [mW/mg]	Curing Peak [°C]
0	34.1	234.2
50	30.8	233.0
100	24.5	230.8
300	20.5	228.3

### 3.3 Thermal Stability

The thermal stability of the polymer synthesized from the benzoxazine monomer radiated at various radiation doses was determined with Thermogravimetric Analyzer (TGA) as presented in Fig. 4 and Table 2. It could be summarized that the degradation temperature and char yield of the polymer synthesized from monomer radiated at low radiation dose (0 to 100 kGy) had no significant change with radiation dose. However, it could be noticed that the char yield and degradation temperature of synthesized polymer derived from monomer radiated at 300 kGy were increased. This could be due to the change in chemical structure of monomer after radiation at such a high radiation dose.

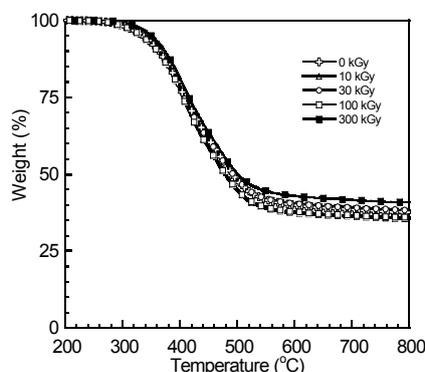


Fig. 4: TGA thermograms of polymer synthesized from benzoxazine monomer radiated at various radiation doses.

Table 2: Degradation temperature and char yield of the polymer synthesized from benzoxazine monomer radiated at various radiation doses.

Radiation Dose (kGy)	Degradation Temperature at 10% weight loss (°C)	Char Yield at 800°C
0	363	38
10	365	36
30	361	38
100	361	36
300	373	40

#### 4. Conclusion

In this study, the curing behaviour and thermal properties of the polymer synthesized from benzoxazine monomer radiated at various radiation doses was investigated. The FTIR spectra of the radiated monomer reveal some chemical change after irradiation. The energy consumption and temperature peak for curing the radiated monomer was reduced with the increase of radiation dose. While the thermal degradation temperature and char yield of the polymer synthesized from the radiated monomer was not changed at low radiation doses, while the values was increased at 300 kGy.

#### 5. Acknowledgement

The authors would like to acknowledge Kasetsart University Research and Development Institute for financial support in the fiscal year of 2010. Additionally, the authors would like to thank Assoc. Prof. Dr. Sarawut Rimdusit for raw material support and Thailand Institute of Nuclear Technology for the use of gamma irradiation machine.

#### 6. References

- [1] X. Ning, and H. Ishida, "Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers," *J. Polym. Sci. Part A: Polym. Chem.* 1994, vol. 32 (6) , pp.1211-1129.
- [2] H. Ishida, and D. J. Allen, "Physical and Mechanical Characterization of Near-Zero Shrinkage Polybenzoxazines," *J. Polym. Sci. Part B: Polym. Phys.* 1996, vol. 34(6), pp.1019-1030.
- [3] H. Ishida, and H. Y. Low, "A Study on the Volumetric Expansion of Benzoxazine-Based Phenolic Resin," *Macromolecules* 1997, vol. 30, pp.1099-1106.
- [4] N. N. Ghosh, B.Kiskan, and Y.Yagci, "Polybenzoxazines-New high performance thermosetting resins: Synthesis and properties," *Prog. Polym. Sci.* 2007, vol. 32, pp.1344-1391.
- [5] S. Rimdusit, V.Jiraprawatthagool, C. Jubsilp, S. Tiptipakorn, and T. Kitano, "Effect of SiC whisker on benzoxazine-epoxy-phenolic ternary systems: Microwave curing and Thermomechanical characteristics," *J. Appl. Polym. Sci.* 2007, vol.105, pp.1968-1977.
- [6] Y. Liu, W. Zhang, Y.Chen, and S. Zheng, " Polybenzoxazine containing polysilsesquioxane: Preparation and thermal properties,"*J.Appl. Polym. Sci.* 2006, vol. 99, pp. 927-936.
- [7] C. Jubsilp, T. Takeichi, and S. Rimdusit, "Effect of novel benzoxazine reactive diluent on processability and Thermomechanical characteristics of bi-functional polybenzoxazine,"*J. Appl. Polym. Sci.* 2007, vol.104, pp. 2928-2938.
- [8] S. Rimdusit, S. Pirstpindvong, W.Tanthapanichakoon, and S. Damrongsakkul, ""Toughening of Polybenzoxazine by Alloying with Urethane Prepolymer and Flexible Epoxy: A Comparative Study," *Polym. Eng. Sci.* 2005, vol. 45, pp.288-296.
- [9] A. Hiroki, H. T. Tran, N. Nagasawa, T. Yagi, and M. Tamada, "Metal Adsorption of Carboxymethyl Cellulose/Carboxymethyl Chitosan Blend Hydrogels Prepared by Gamma Irradiation," *Radiat Phys Chem*, 2009, vol.78 (12), pp.1076–1080.

- [10] S. Jipa, T. Zaharescu, R. Setnescu, E.S. Dragan, and M.V. Dinu, "Thermal and Radiochemical Degradation of some PAN copolymers," *Mater. Chem. Phys.*, 2008, vol. 112 (2), pp.612–616.
- [11] T. Li, H.G. Park, and S.H. Choi, "Gamma-irradiation-induced preparation of Ag and Au nanoparticles and their characterizations," *Mater. Chem. Phys.*, 2007, vol.105 (2–3), pp.325–330.
- [12] R.L. Clough, "High-energy radiation and polymers:a review of commercial processes and emerging applications," *Nucl. Instrum.Methods Phys. Res., Sect. B*, 2001, vol. 185, pp. 8–33.
- [13] N. Salah, S.S Habib, Z.H. Khan, S. Al. Hamedi, and F. Djouider, "Functionalization of gold and carbon nanostructured materials using gamma-ray irradiation," *Radiat. Phys. Chem.* 2009, vol. 78 (11), pp.910–913.
- [14] Ishida, H. U.S. Pat. 5,543,516 (1996).