Physical Characterizations and Hardness of Polymers Obtained from Irradiated Benzoxazine Monomer

Sunan Tiptipakorn

Abstract—**In this research, benzoxazine monomer was irradiated with gamma ray at various radiation doses, i.e. 0, 30, 100 and 300 kGy. The synthesized polymers were obtained by heating without need of catalyst. The curing behaviors 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 consumption during polymerization. Furthermore, the temperature 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 300 kGy. In addition, the results reveal that the amount of water uptake of polymers obtained from radiated monomer was significantly low, whereas the hardness of the polymer synthesized from monomer radiated at 300 kGy was higher than the polymer synthesized from non-radiated monomer.**

Index Terms—**Benzoxazine, gamma irradiation, hardness, water uptake.**

I. 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 studied and compared with the pristine polymer. Moreover, the physical properties such as water absorption and density of the polymer as well as their hardness were also determined.

II. EXPERIMENTAL

A. 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.

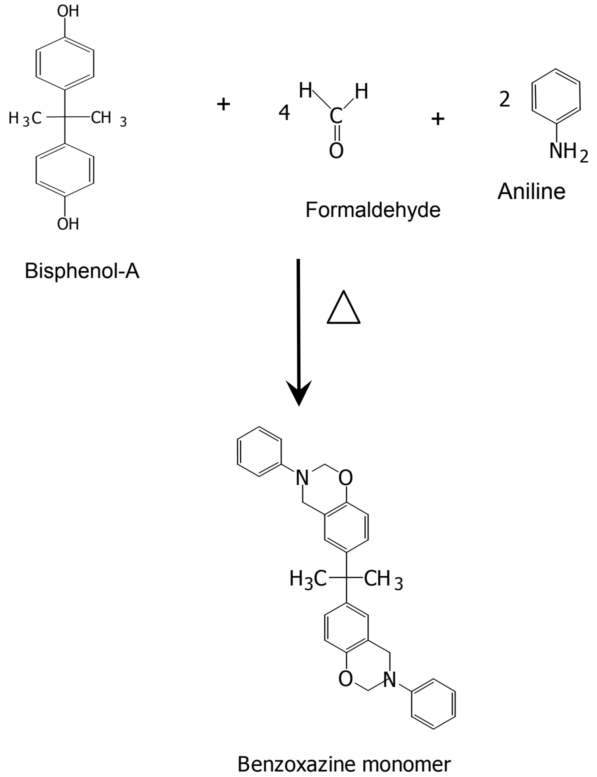

Fig. 1. Synthesis method of benzoxazine monomer.

B. Benzoxazine Monomer Synthesis

Three raw materials (bisphenol-A, aniline, and paraformaldehyde) were mixed using the patented solventless technology in order to synthesize the benzoxazine monomer [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

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without purification. The method to synthesize benzoxazine monomer is illustrated in Fig. 1. From this method, no by-product as well as volatile was generated in the samples.

C. *Polymer Preparation*

The polymer was obtained from polymerization by heating benzoxazine monomer, which was irradiated at various radiation doses (0, 30, 100, 300 kGy) with dose rate of 8 kGy/hour under nitrogen atmosphere. After irradiation, the heating program of polymerization of 150°C, 200 °C, and 240°C (for 2 hours at each temperature) was performed. The red-brown and transparent polymers were obtained after full polymerization.

D. *Sample Characterizations*

In order to obtain the change of chemical structure after radiation, 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^{-1}.

Curing temperatures of the polymer synthesized from monomer 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).

The densities of the radiated monomer and polymer were measured by a water displacement method as ASTM D792–91 (Method A).

Water absorption measurement was conducted by water immersion for 7 days. Based on the initial conditioned mass of each specimen, the amount of water absorbed was calculated from the following formula:

$$\textit{Water Absorbtion}\,(\%) = \frac{M_t - M_o}{M_o} \times 100 \qquad (1)$$

where M_t and M_o is mass of specimen after and before immersion, respectively.

Weight difference measurement after acetone immersion for 7 days was carried out. The percentage of weight difference could be calculated as follows:

$$\textit{Weight Difference}\,(\%) = \frac{M_t - M_o}{M_o} \times 100 \qquad (2)$$

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.

Microhardness of compressed specimens was measured utilizing a Vickers microhardness tester (model FM-700C) from Future-Tech. A pyramidal diamond was applied to the surface of the composite under a load of 9.80 N for 15 s. Diagonal length of the indentation was measured through a micrometric eyepiece with objective lens (500x magnifications). Each sample was measured repeatedly for ten times.

III. RESULTS AND DISCUSSION

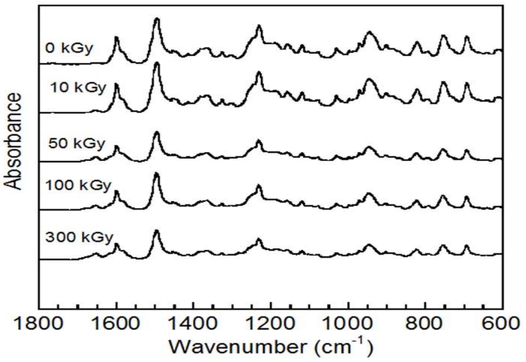

Fig. 2. FT-IR spectra of monomer radiated with various radiation doses.

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^{-1} (aromatic ring), 1323 cm^{-1} (C-O stretching), and 1350-1000 cm^{-1}(C-N stretching) were reduced especially in high radiation doses. It could be assumed that some chemical chains in benzene ring were possibly broken.

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 I. It could be noticed that the temperature of curing peak and heat of curing were decreased with the increase of radiation dose. Fig. 3 and Table I could present the advantage of the gamma radiation for lowering the curing temperature of the monomer, indicating lower energy consumption for polymerization.

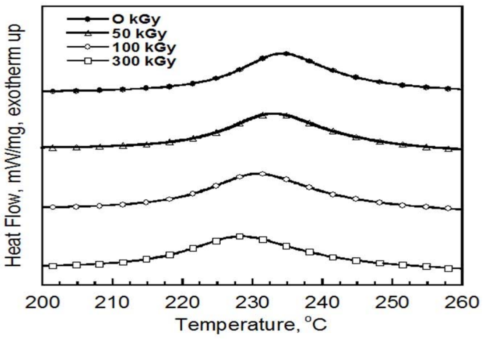

Fig. 3. DSC thermograms of monomer radiated with various radiation doses.

TABLE I: 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

The densities of irradiated monomer and those of polymer obtained from benzoxazine monomers radiated at various radiation doses were illustrated in Fig. 4 and Fig. 5, respectively. It could be noticed that the radiation dose could lead to lower the density of the radiated monomer and the obtained polymer (Table II). From the literature [15], the densities of typical benzoxazine monomer and polybenzoxazine based on aniline were reported to be 1.200 and 1.195 g/cm^3, respectively.

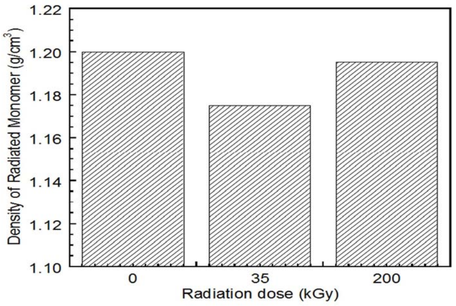

Fig. 4. Density of radiated monomer.

Water absorption measurements of the samples were performed; the results are shown in Fig. 6. It could be noticed that the radiation dose at 300 kGy could provide the lowest amount of water uptake, while the specimen obtained from monomer at 100 kGy could absorb the highest amount of water. However, the amounts of water uptake for all specimens are in the low range, i.e. less than 1.5 wt% after 7 days of water immersion.

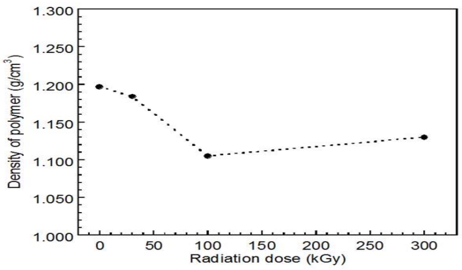

Fig. 5. Density of polymer obtained from radiated monomer.

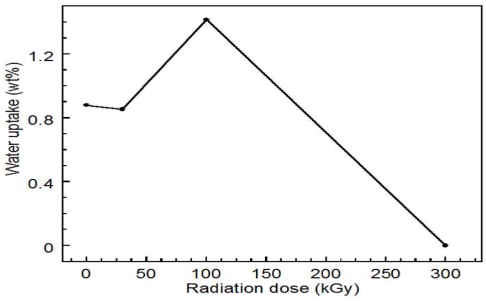

Fig. 6. Water uptake of polymer synthesized from radiated monomer.

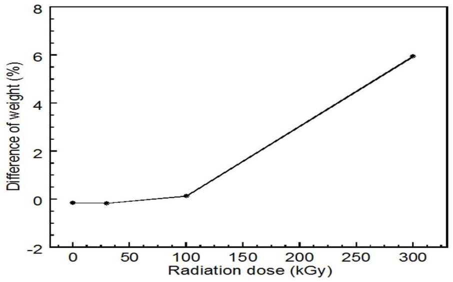

Fig. 7. Weight difference of polymer after acetone immersion for 7 days

Figure 7 exhibits the weight difference after acetone immersion. It could be noticed that the polymer obtained from monomer radiated at low radiation dose have no significant change in weight. However, for the case of 300 kGy, the difference of weight was obviously found. This could be due to the fact that the network structure change at high radiation dose leads to swelling behaviors.

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. 8 and Table III. 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.

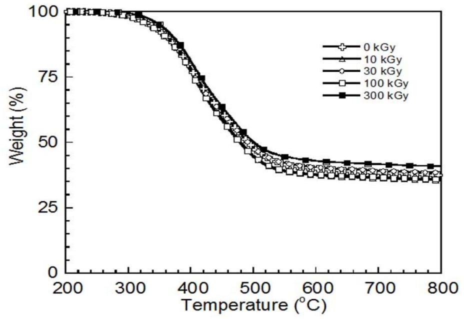

Fig. 8. TGA thermograms of polymer synthesized from benzoxazine monomer radiated at various radiation doses.

TABLE II: EFFECT OF GAMMA RADIATION ON THE DENSITY OF BENZOXAZINE MONOMER.

Radiation dose (kGy)	Density of radiated monomer (g/cm^3)
0	1.200
35	1.175
200	1.195

TABLE III: 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

The derivative thermograms of thermogravimetric analysis (DTG) for the polymer synthesized form monomer radiated at 0, 30 and 300 kGy are shown in Fig. 9-11, respectively. It could be noticed that the polymer of the polymer in case of 300 kGy provide the fluctuation in the weight loss, while that of 0 kGy is rather smooth.

After deconvolution of the DTG curves, it could be observed that the polymer in case of non-radiated monomer (Fig. 12) provides 3 main sub-stages of thermal decomposition [16], while that in case of 300 kGy (Fig.13) provides at least 4 main sub-stages of thermal decomposition.

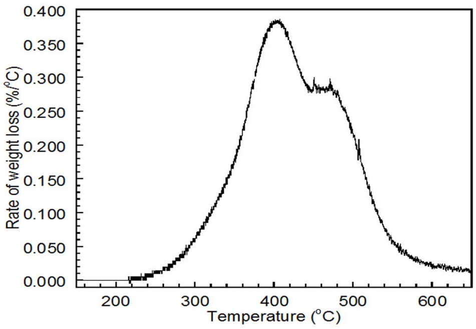

Fig. 9. DTG thermograms of polymer synthesized from benzoxazine monomer without radiation

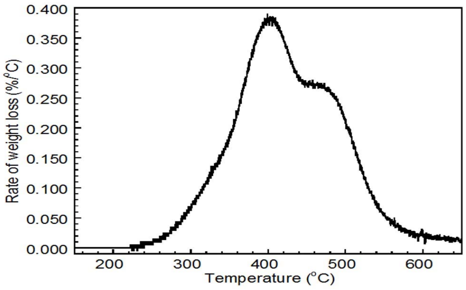

Fig. 10. DTG thermograms of polymer synthesized from benzoxazine monomer radiated at 30 kGy.

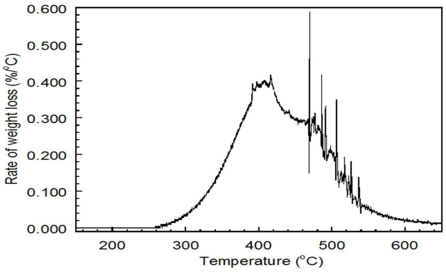

Fig. 11. DTG thermograms of polymer synthesized from benzoxazine monomer radiated at 300 kGy.

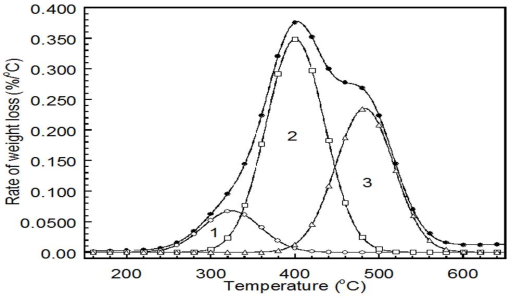

Fig. 12. Three main sub-stages of thermal decomposition of the polymer in case of non-radiated monomer.

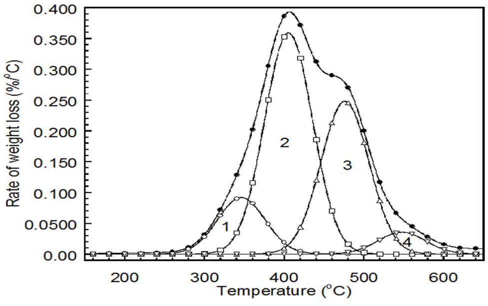

Fig. 13. Four main sub-stages of thermal decomposition of the polymer in case of monomer radiated at 300kGy.

The peaks of decomposition temperature of each sub-stage are presented as seen in Table IV. It could be noticed that the peak at stage 1 in case of 300 kGy is significantly higher than that in case of 0 kGy.

TABLE IV. COMPARISON OF TEMPERATURE AT PEAK OF EACH SUB-STAGE.

Radiation Dose (kGy)	Temperature of peak at each sub-stage (°C)			
	Sub-stage 1	Sub-stage 2	Sub-stage 3	Sub-stage 4
0	324.9	400.6	483.1	-
300	346.3	405.4	476.2	547.8

The microhardness values of the specimens are shown in Fig.14. It could be seen that at low radiation dose such as 30 kGy, the microhardness of the specimen was not different from the polymer synthesized from non-radiated monomer; the value was in the range of error bar. However, the radiation dose at 300 kGy could provide significant enhancement of microhardness of the polymer.

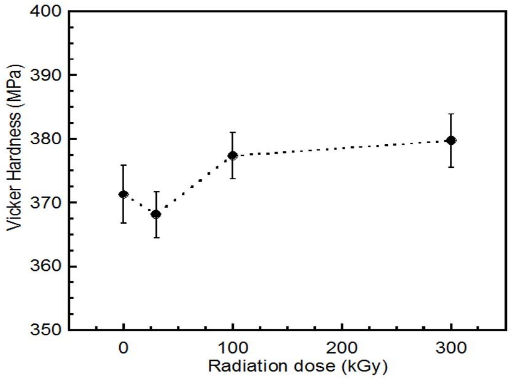

Fig. 14. Microhardness of polymer synthesized from radiated monomer.

IV. CONCLUSION

The curing behavior, physical and thermal properties as well as hardness of the polymer synthesized from benzoxazine monomer radiated at various radiation doses were determined in this study. The FTIR spectra of the radiated monomer reveal some chemical change after irradiation. The energy consumption and temperature peak for polymerization of the radiated monomer was reduced with the increase of radiation dose. The density of radiated monomer and obtained polymer synthesized from radiated monomer as well as the amount of water uptake of polymer obtained from the radiated monomer were lower than those of polymer synthesized from non-radiated monomer. From the TGA results, 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 were increased at 300 kGy. The results of micro-hardness test reveal that the radiation dose at 300 kGy to the monomer could increase the hardness of the obtained polymer.

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