The Thermal and Mechanical Properties of Electron Beam-Irradiated Polylactide

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Abstract - The effect of electron beam irradiation on the thermal and mechanical properties of polylactide (PLA) was investigated in this research. PLA films were irradiated by electron beams at different absorption doses ranging from 20 to 200 kGy. The thermal and mechanical properties of the irradiated PLA films were investigated by means of differential scanning calorimeter, thermogravimetric analyzer, universal testing machine, dynamic mechanical analyzer, and thermal mechanical analyzer. The results revealed that the chain scission of the PLA predominated over the crosslinking during the irradiation, which considerably deteriorated the thermal and mechanical properties of the PLA.

Key words : Electron beam, Thermal and mechanical properties, Polylactide

INTRODUCTION

Radiation processing has been widely utilized to modify conventional polymers in various industrial fields because it offers several advantages over other modification methods such as an eco-friendly process, a precise controllability, no additives, a temperature-independence, and a low energy consumption (Clenland *et al.* 2003; Chimelewski *et al.* 2005). This processing generally is based on the crosslinking, degradation, and graft polymerization induced by high energy irradiation.

In the last few years, it has been demonstrated that the radiation processing of biodegradable polymers is convenient, eco-friendly, and commercially-attractive (Haji-Saeid *et al.* 2007). Thus, radiation processing has been explored to alter the physical and chemical characteristics of various biodegradable polymers such as polylactide, poly(butylene succinate), poly(3-hydroxybutyrate), poly(ε-caprolactone) (PCL), etc (Sodergard 2004).

Among the biodegradable polymers, polylactide (PLA) has been considered as one of the most promising biodegradable polymers for the substitution of non-biodegradable conventional polymers due to its processability and good biodegradability. Nonetheless, its brittleness, low thermal instability, and low flexibility has limited its diverse applications (Bhardwaj and Mohanty 2007; Kumara *et al.* 2008). Thus, numerous research activities on the modification of the PLA by using radiation has been carried out to modify the properties of PLA (Jin *et al.* 2002; Milicevic *et al.* 2007; Jia *et al.* 2009). However, the multilateral study on the effect of electron beam irradiation on the thermal and mechanical properties of PLA has rarely been carried out.

In this study, the changes in the thermal and mechanical properties of PLA brought about by electron beam irradiation was investigated. PLA films prepared by a solvent-casting method were irradiated by electron beams at various absorption doses. The resulting films were investigated in terms of crosslinking degree, thermal, mechanical, and viscoelastic properties by using differential scanning calorimeter, ther-

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mogravimetric analyzer, universal testing machine, dynamic mechanical analyzer, and thermo-mechanical analyzer.

MATERIALS AND METHODS

1. Preparation of polylactide films

Biodegradable polylactide (PLA, Grade: 4032D) was purchased from NatureWorks and chloroform supplied from Showa Chemicals was used as a solvent. PLA films were obtained by casting a 10 wt% PLA solution in chloroform on well-cleaned glass substrates and drying in air at room temperature for slow evaporation. The dried films were further dried in a vacuum oven for 24 h. The thickness of the resulting PLA films was around 130 μm.

2. Electron beam irradiation

The prepared PLA films were put into aluminum pouches and thermally sealed after purging with nitrogen gas. Electron beam irradiation was performed at room temperature by using an ELV-3 e-beam accelerator installed at EB-Tech (Daejeon, Korea). The energy and current density of the electron beams were 2.0 MeV and 1.0 mA cm^{-2}, respectively. The total absorption dose ranged from 20 to 200 kGy. After irradiation, the samples were kept in a vacuum oven at 80°C for 2 h to remove the remaining radicals. The crosslinking degree of the irradiated PLA films was determined by measuring the amounts of the insoluble materials in chloroform.

3. Characterization

The glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures were measured by using a differential scanning calorimeter (DSC, TA instrument, Q1000) between 0 to 200°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The degree of crystallinity (X_c) was calculated as the percentage of the fusion enthalpy of the tested PLA samples over the fusion enthalpy of the 100% crystalline PLA, 135.0 J g^{-1} (Milicevic *et al.* 2007). The thermogravimetric analysis (TGA) was carried out using an SDT Q600 analysis system (TA Instrument, USA) between 50 to 700°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The decomposition temperature (T_d) in this measurement was defined as the 5% mass loss temperature. The tensile properties such as tensile strength, tensile modulus, and elongation-at-break were measured by using a universal testing machine (UTM, Instron Model-4210, Instron Engineering Co., USA) according to the ASTM Standard D638. The dynamic mechanical properties were investigated by using dynamic mechanical analyzer (DMA, Q800 model, TA instrument) under a film-tension mode in a temperature range of 0 to 200°C at a heating rate of 2°C min^{-1} and a frequency of 1 Hz. The thermomechanical analysis (TMA) was performed on a TMA Q400 analysis system (TA Instrument, USA) using an film extension probe between 20 and 200°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere.

RESULTS AND DISCUSSION

The crosslinking degree of the irradiated PLA films at different absorption doses was measured to investigate the formation of network structures in the PLA by electron beam irradiation that could have any considerable effect on the thermal and mechanical properties of the PLA. However, all the irradiated PLA films at the given absorption doses were clearly dissolved in an extraction solvent and thus their crosslinking degree could not be measured (the data not shown), indicating that the PLA was not crosslinked by electron beam irradiation.

The DSC thermograms of the control and irradiated PLA films are shown in Fig. 1 and Table 1. As shown in Fig. 1, all the DSC heating curves showed three thermal transition

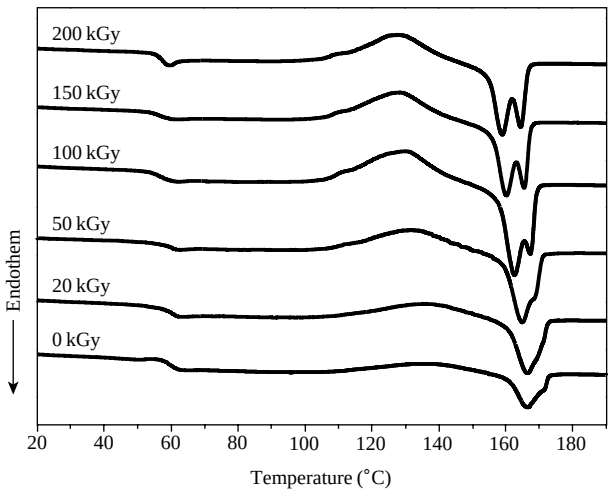

Fig. 1. DSC heating curves of the control and irradiated PLA films at various absorption doses.

Table 1. The thermal properties of the control and the irradiated PLA films

Absorption dose (kGy)	T_g (°C)	T_c (°C)	T_m (°C)	X_c (%)
0	63.4	136.1	166.4	10.81
20	62.3	135.7	116.0	17.2
50	62.0	131.6	164.8	22.82
100	60.2	129.7	162.5	31.58
150	59.8	127.4	160.3	25.73
200	58.1	127.0	158.9	25.13

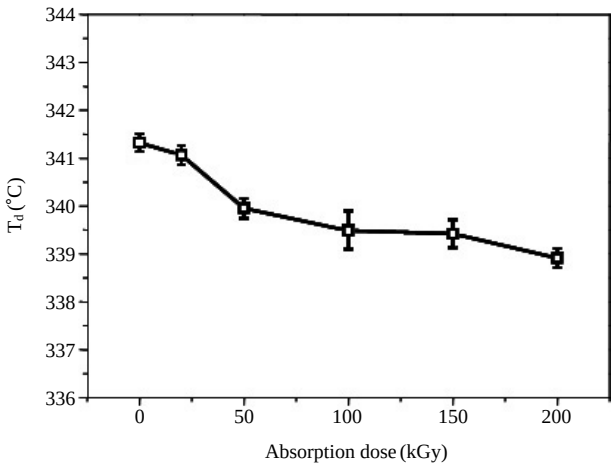

Fig. 2. The decomposition temperatures (T_d) of the PLA as a function of the absorption dose.

peaks corresponding to the T_g, T_c, and T_m of PLA. Those three transition temperatures of the irradiated PLA films were gradually decreased with an increasing absorption dose when compared to those of the control PLA film as presented in Fig. 1 and Table 1. These results could be explained by the fact that the chain scission of the PLA chains during the irradiation gave rise to the shorter polymer chains with the better mobility which could have the more significant effect on the transition temperatures of the PLA. Moreover, the crystallinity of the irradiated PLA films increased with an absorption dose up to 100 kGy, above which it decreased. These changes in the crystallinity could be explained as follows: at a lower absorption dose up to 100 kGy, the shorter PLA chains generated by radiation-induced chain scission were reoriented and thus leading to the increase in the crystallinity. However, at a higher absorption dose, the decrease in the crystallinity can be attributed to the destruction of the crystalline domains in the PLA by free radicals generated by electron beam irradiation (Loo *et al.* 2005).

The thermal stability of the control and irradiated PLA films was investigated by the TGA analysis in nitrogen atmosphere and the results are shown in Fig. 2. The thermal degradation of all the samples underwent the one-stage weight loss. The T_d of the control PLA was 341.4°C. In the case of the irradiated PLA films, the T_d decreased with an increasing absorption dose in comparison with that of the control PLA. This reduction in the thermal stability of the irradiated PLA films could be explained by the fact that the chain scission of the PLA predominated over the cross-linking during irradiation, and thereby generating the shorter PLA chains which could be more liable to the thermal decomposition.

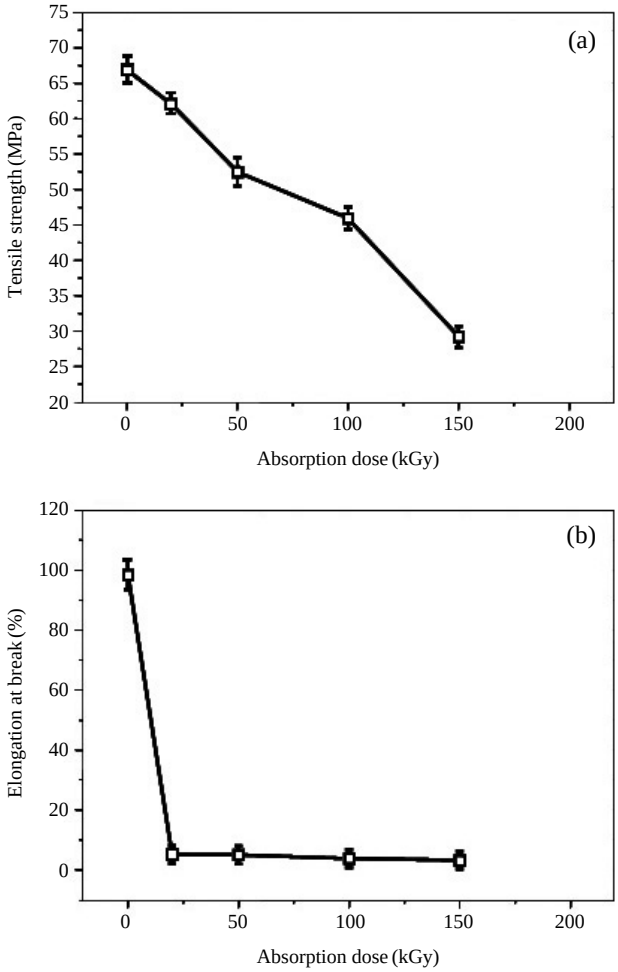

Fig. 3. The tensile strength (a) and elongation-at-break (b) of the PLA as a function of the absorption dose.

The tensile properties of the control and irradiated PLA films as a function of the absorption dose are shown in Fig. 3. The tensile properties of the irradiated PLA films at 200 kGy could not be measured due to its high brittleness. As

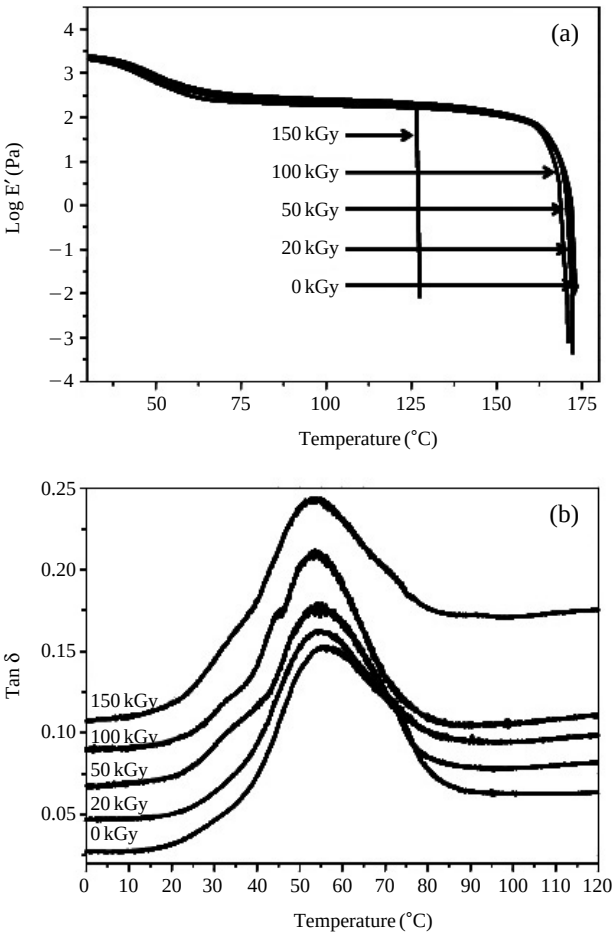

Fig. 4. The storage modulus (a) and tan δ (b) of the control and irradiated PLA films at various absorption doses.

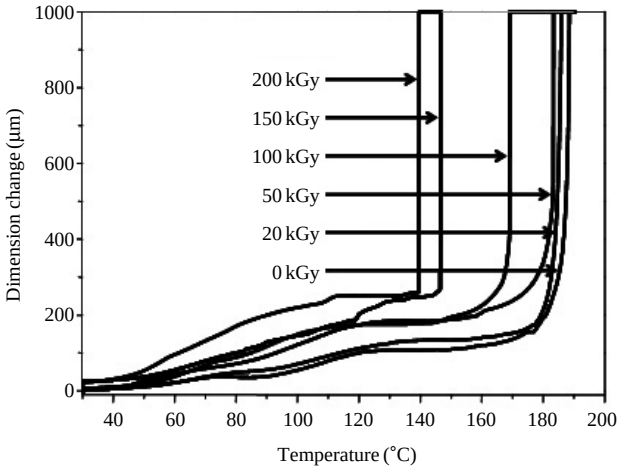

Fig. 5. The TMA heating curves of the control and irradiated PLA films at various absorption doses.

shown in Fig. 3(a), the tensile strengths of the irradiated PLA films were gradually increased with an increasing absorption dose in comparison to that of the control PLA. Likewise, as presented in Fig. 3(c), the elongation property of the irradiated PLA films showed the similar tendency as the tensile strength but it abruptly dropped even at 20 kGy, indicating that the elongation property of the PLA is more sensitive to electron beam irradiation. This reduction in the mechanical properties could be interpreted as follows: tie molecules connecting the crystallites in the amorphous regions could be randomly degraded during irradiation and therefore leading to the increase in the brittleness of the PLA that could be responsible for the reduction in the tensile strength and elongation-at-break of the PLA (Medel 2005).

The storage modulus and tan δ of the control and the irradiated PLA films at different absorption doses are presented in Fig. 4. The DMA analysis for the irradiated PLA films at 200 kGy was not performed due to their high brittleness as mentioned above. As shown in Fig. 4(a), the rubbery plateau regions of the irradiated PLA films were gradually shortened with an increasing absorption dose when compared to that of the control PLA. This result could be ascribed to the increase in the brittleness of the irradiated PLA films caused by the radiation-induced chain scission. Furthermore, as shown in Fig. 4(b), the temperature at the maximum peak of the tan δ, associated with the T_g of the PLA, was gradually shifted to a lower temperature with an increasing absorption dose because of the radiation-induced chain scission as mentioned in the DSC results.

The thermomechanical analysis of the control and the irradiated PLA films at different absorption doses is shown in Fig. 5. The control PLA revealed typical two transition temperatures: the T_g of 58°C and the T_m of 175°C. On the other hand, in case of the irradiated PLA films, the two transition temperatures were gradually moved to a lower temperature, suggesting that the PLA was degraded during irradiation.

CONCLUSION

The changes in the thermal and mechanical properties of the biodegradable PLA by electron beam irradiation were investigated in this study. The result of the crosslinking degree measurement showed that the PLA was not crosslinked by electron beam irradiation. The results of the thermal and mechanical analyses showed that the thermal and me-

chanical properties of the PLA were reduced after electron beam irradiation and the extent of the reduction was definitely dependant on the absorption dose. This reduction could be ascribed to the fact that the chain scission of the PLA predominated over the crosslinking during irradiation, which considerably deteriorated the thermal and mechanical properties of the PLA.

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