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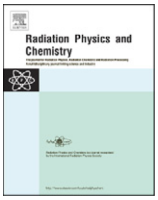

Degradation behavior of poly (L-lactide-co-glycolide) films through gamma-ray irradiation

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ABSTRACT

Gamma-ray irradiation is a very useful tool to improve the physicochemical properties of various biodegradable polymers without the use of a heating and crosslinking agent. The purpose of this study was to investigate the degradation behavior of poly (L-lactide-co-glycolide) (PLGA) depending on the applied gamma-ray irradiation doses. PLGA films prepared through a solvent casting method were irradiated with gamma radiation at various irradiation doses. The irradiation was performed using 60Co gamma-ray doses of 25–500 kGy at a dose rate of 10 kGy/h.

The degradation of irradiated films was observed through the main chain scission. Exposure to gamma radiation dropped the average molecular weight (M_n and M_w), and weakened the mechanical strength. Thermograms of irradiated film show various changes of thermal properties in accordance with gamma-ray irradiation doses. Gamma-ray irradiation changes the morphology of the surface, and improves the wettability. In conclusion, gamma-ray irradiation will be a useful tool to control the rate of hydrolytic degradation of these PLGA films.

1. Introduction

Polymer degradation generally occurs via a scission of the main or side polymer chains, and is induced through photodegradation, oxidation, or hydrolysis. The degradation of certain polymers takes place in biological environments including soil and water, as well as within the bodies of humans and animals. These polymers have been applied to various biomedical fields, e.g., drug delivery, gene delivery, and tissue engineering (Fugita, 2003). Recently used biodegradable polymers include polyesters, and their copolymers. Aliphatic polyesters of both natural and synthetic origins are among the biodegradable polymers that have been most intensively investigated (Garkhal et al., 2010; Shin et al., 2010; Lee et al., 2011).

Polyesters that include a hydrolysable ester bond in their backbone are considered the best biomaterials with regard to their design and performance. Polyesters are biocompatible, biodegradable, and non-toxic materials. Their products of degradation are also biocompatible and are eliminated from the body through either the respiratory or urinary systems. Polyesters degrade through a hydrolytic attack of the ester bond (Fugita, 2003; Lee et al., 2011).

Polyester polymers are all hydrolytically unstable. In the case of PCL (poly(ε-caprolactone)), while they are enzymatically degradable in earth environments, in living bodies, they are non-enzymatically degradable. Poly (L-lactic acid), on the other hand, is non-enzymatically degraded both in earth environments and in living bodies. Polyesters degrade through a hydrolytic cleavage of their ester bonds. In the human body, lactic and glycolic acids enter Kreb's cycle as hydrolysates and are metabolized. Afterwards, they are removed from the human body as carbon dioxide and water (Loo et al., 2004).

Radiation technology is a very useful process in biomedical applications (Lim et al., 2010). Before using radiation for the sterilization of biomedical devices, it is necessary to decide whether the radiation process may have an effect on the materials used in the devices. The high-energy radiation treatment causes alterations in polymeric material and the chemical properties of polymers (Birkinshaw et al., 1992). The effects of high-energy radiation on polymers are generally divided into main chain scission (degradation) and crosslinking (polymerization). Although both the processes take place simultaneously in many polymers, if the scission predominates the crosslinking, it is termed a degradation process. Polymer degradation, where chain scission is dominant, is associated with a reduction in the molecular weight. On the other hand, crosslinking results in an increase in the molecular weight. Active species from radiation,

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such as cations, anions and radicals, can react with one another, or are able to initiate further reactions among the polymeric chains, thus giving rise to changes in material properties. As a consequence, cross-linking reactions or the chain scission through the breading of chemical bonds can occur, depending on the radiation dose. In general, aromatic polymers are more resistant to sterilization by high-energy radiation than aliphatic polymers, while the presence of impurities and additives may enhance degradation and/or crosslinking (Suljovruji et al., 2003).

The responses of biodegradable aliphatic polyester to radiation depend on the presence or absence of methyl side group. Main chain scission occurs predominantly by the irradiation of poly (hydroxy buthylate) (PHB) (Mitomo et al., 1995) and PLLA (Pramono et al., 2001) that have methyl groups. While, polyesters such as poly (ε -caprolactone) (PCL) (Darmawan et al., 1998) and poly (butylene succinate) (PBS) (Song et al., 2001) that have no methyl group are radiation crosslinkable. The degradation rate of polymeric biomaterials due to γ-ray irradiation is linked to radical formation (Martínez-Sncho et al., 2004).

The aim of this work was to investigate the effects of gamma-ray irradiation on poly (L-lactide-co-glycolide) (PLGA), including hydrophilicity, mechanical strength, chemical composition and surface morphology.

2. Experimental

2.1. Materials

Biodegradable polymers, Poly (L-lactide-co-glycolide) (PLGA 85/15), was purchased from RESOMER® (Boehringer Ingelheim Pharma GmbH &Co.KG, Germany) (Fig. 1). Chloroform ($CHCl_3$, Showa Co. Ltd., Japan) was selected as a solvent.

2.2. Preparation of the polymer films

Polymer films were prepared using a solution casting method. PLGA (2 wt%) was dissolved in chloroform which was used as a solvent. The polymer solutions were then casted onto a well-cleaned glass plate. After solvent evaporation in air at room temperature, the films were separated from the glass plates and dried in a vacuum oven at room temperature, for 24 h. For gamma-ray irradiation, the prepared films were packed in aluminum sealing bag with nitrogen gas. The gamma-ray irradiation was carried out using a ^{60}Co source (MDS Nordion, Canada, IR 221 n wet storage type C-188, KAERI). The total dose ranged from 25 kGy up to 500 kGy with a dose rate of 10 kGy/h.

2.3. ATR-FTIR measurement

ATR spectra for biodegradable polymers irradiated with gamma-ray were obtained using an ATR-FTIR spectrophotometer (Bruker TEMSOR37, Bruker AXS. Inc., Germany). The spectra were measured in the region of 500–4000 cm^{-1} at a resolution of 4 cm^{-1} in the ATR mode.

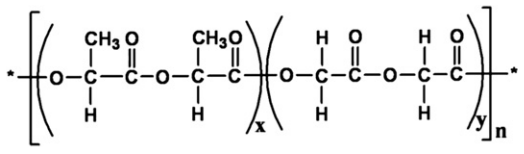

Fig. 1. Structures of PLGA.

2.4. Thermal properties

The thermal properties of the polymer films were recorded through a difference scanning calorimetry (DSC). DSC thermograms of the obtained films were measured using a DSC Q100 TA instrument in the temperature range from -50 to 250 °C in a nitrogen atmosphere; the heating rate was 5 °C/min. Then, the sample pans were cooled at room temperature. The second run heating was observed for these samples from -50 to 250 °C.

2.5. Average molecular weight

Molecular weights were determined using a gel permeation chromatography (GPC, PL-GPC110, Polymer Laboratories Ltd., UK) equipped with columns of PL gel Guard column 5 μm, PL gel 10 μm Mixed B and PL gel 5 μm 10,000 A (Polymer Laboratories Ltd., UK) calibrated with polystyrene. Chloroform was used as a mobile phase at a flow rate of 1.0 ml/min at 40 °C.

Variation in molecular weight is related to the radiation chemical yields of crosslinking (G_x) and chain scission (G_s), which determines the extent of chain scission or crosslinking during gamma-ray irradiation, and can be calculated from the following equations (Şen et al., 2003):

$$1/M_w = 1/M_{w,0} + (G_s/2 - 2G_x)D_x 1.038 \times 10^{-6} \qquad (1)$$

$$1/M_n = 1/M_{n,0} + (G_s - G_x)D_x 1.038 \times 10^{-6} \qquad (2)$$

where $M_{w,0}$ and $M_{n,0}$ are the molecular weight and number of average molecular weight of unirradiated films.respectively. M_w and M_n are the corresponding values following exposure to irradiation dose, D_x (unit: kGy). A G_s/G_x ratio of greater than 4 would indicate that chain scission is more prominent (Şen et al., 2003). Eq. (1) can be applied for any initial molecular weight distribution of the polymer, but Eq. (2) can only be applied for an initial most probable distribution ($M_w/M_n = 2$). Since the M_w/M_n of the used PLGA is about 1.3, obtained G values by these equations are approximated values.

2.6. Mechanical properties

The mechanical property of the films was measured based on ASTM D 882 using a Universal Tensile Machine (Instron Model-4443). All films had a gage length of 31.8 mm, width of 5.3 mm and different thicknesses of 30–40 μm, and were stretched at a crosshead speed of 50 mm/min.

2.7. Surface characterization

The surface morphology of the prepared samples was first examined using a field-emission scanning electron microscope (Jeol JSM-6390, Jeol Ltd., Japan). The film pieces were coated with a 40–50 nm layer of gold using a metal ionizer (Jeol FineCoat Sputter JFC-1100, Jeol Ltd., Akishima, Japan), allowing surface and cross-section visualization. All the samples were examined at an accelerating voltage of 1 kV.

The contact angles of tater on the polymer film surfaces after gamma-ray irradiation were measured at room temperature using a contact-angle meter (Phoenix-300, Surface electro optics Ltd., Korea).