Study of the effect of electron beam on thermal and mechanical properties of poly(lactic acid)/poly(butylene succinate) blends

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Abstract. In this research, the effect of radiation dose on thermal and mechanical properties of polymer blends between poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) were determined at the PLA/PBS weight ratios of 100/0, 80/20, and 0/100. Dicumyl peroxide (DCP) was used as additive at 0.2 phr. The radiation doses were varied at 0-150 kGy. There were some changes of chemical structure upon irradiation as observed via Fourier Transform Infrared Spectrometer (FT-IR), leading to the decrease of melting temperature (T_m) with the increase of radiation doses. Moreover, the flexural strength determined via Universal Testing Machine (UTM) were decreased with increasing radiation doses. The lowest biodegradation was found at the radiation dose of 50 kGy.

1. Introduction

The use of plastic from petroleum in the recent years has led to serious environment pollution due to their non-biodegradability. Biodegradable plastic has attracted most interest because of more environmentally awareness. Especially, biodegradable polyester contains numerous ester linkage which can be easily hydrolysed by water. Poly(lactic acid) (PLA), poly(butylene succinate) (PBS), polycaprolactone (PCL) and polyhydroxyalkanoate (PHA) are such well known as excellent biodegradability aliphatic polyesters.

PLA has been widely used to substitute conventional plastic due to various outstanding characteristics for example great tensile modulus and flexural modulus over high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS). However, low elongation at break and impact strength of PLAs are their main drawbacks [1]. Moreover, PLAs have low thermal and dimensional stabilities under high temperature. To improve those mentioned properties, the crosslinking technique has been applied. PBS is also one kind of aliphatic biodegradable polyester to as PLA. PBS has gained much interesting due to its good impact strength, high flexibility and excellent thermal properties (degradation temperature of 399˚C). The applications of PBS include food container, plastic bottle and food-graded film. PBS is widely used to improve properties by blending or blend to other polymers.
The blend of PLA/PBS has been developed using dicumyl peroxide (DCP) as radical initiator using reactive blending [2]. By this procedure, it is believed that the partial miscible blend of the PLA/PBS occurred as evidenced of some degree of crosslinking and branching between PLA and PBS molecules. Moreover, it was reported that the DCP content of 0.2 and 0.3 phr provided the greatest properties of PLA/PBS.

The objective of this research is aimed to develop mechanical and thermal properties of PLA by blending with high flexibility and thermal stability PBS using DCP as compatibilizer. The effects of various PLA/PBS blending weight ratios and radiation doses on thermal and mechanical properties of PLA/PBS blend were investigated.

2. Experiment

2.1 Materials and polymer preparation

Raw materials used in this research were PLA and PBS. PLA (Ingeo Biopolymer 3052D) having molecular weight of 180,000 dalton was supplied by NatureWorks. PBS (BioPBSTM FZ91PM, density of 1.26 g cm\(^{-3}\)) and dicumyl peroxide (98% AR grade) were purchased from Sigma Aldrich Co.

2.2 Preparation of the polymer blend

Both PLA and PBS pellets were initially dried in an air-circulated oven at a temperature of 50˚C for 2 hours to remove moisture before processing and kept in a desiccator at a room temperature. The PLA and PBS having weight ratios of 100/0, 80/20 and 0/100 were then mixed with 0.2 phr of DCP via an internal mixer at a temperature of 170˚C for 10 minutes. The mixed polymer was hot pressed into a test specimen using a hydraulic compression molder (model PR1D-W300L300 HD). An electron beam radiation was carried out at various radiation doses of 0, 50, 100 and 150 kGy.

2.3 Characterization of the polymer blend

Chemical structure and network formation of a sample was studied by Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectra of all samples were acquired by a FT-IR spectrometer from Bruker Tensor 27. All spectra were taken as a function of time with 512 scans at a resolution of 4 cm\(^{-1}\) and a spectral range of 2000-800 cm\(^{-1}\).

A differential scanning calorimeter (DSC) model DSC822e from Mettler Toledo, was used to study melting temperature (T\text{m}) of the PLA/PBS blend. All samples were put in 40 µl aluminum pans with lids. The sample with a mass in a range of 5-10 mg was sealed in an aluminum pan. The DSC thermogram was obtained using a heating rate of 20˚C min\(^{-1}\) from temperature at -60˚C to 200˚C under a constant flow of nitrogen of 60 ml min\(^{-1}\).

A universal testing machine (model 5567) from Instron Co., Ltd. was used to measure flexural strength and modulus of the blends according to ASTM D 790M-94. The test method used was a three-point bending mode with a support span of 48 mm at a constant cross head speed of 1.2 mm min\(^{-1}\). The dimension was 25 mm in width, 60 mm in length, and 2 mm in thickness. The average value from three samples was reported.

Biodegradability of the PLA/PBS blends was carried out using specimen with 12.7 mm in length and 3.3 mm in width. The specimens were buried into the 20 mm depth of soil having pH of 7.43 and moisture of 65.99%. The samples were then weighed for every ca. 7 days for total period of 28 days.

3. Results and Discussion

3.1 Chemical structure of the PLA/PBS blends

The FTIR spectra of the PLA/PBS blend at 80/20 at various radiation doses is illustrated as shown in figure 1. It was noticed that changes in the absorption peak characteristics of PLA after electron beam radiation at 0-150 kGy was observed. The appearance of absorption peaks at 1757, 1088 and 2994 cm\(^{-1}\) assigned to the C=O stretching and C-O stretching of ester group and C-H stretching of the blends,
respectively. These characteristic peaks were similar to those of previous report [3]. Polymer chain scissoring and crosslinking mechanisms were believed to occur at the same time during electron beam radiation as seen from the changes in transmittance of ester linkage and C-H stretching. Moreover, a small shoulder at 1663 cm\(^{-1}\) assigned to C=C was noticed from the PLA/PBS blend indicating the C=C was generated after radiation.

**Figure 1.** FT-IR Spectrum of PLA/PBS blend at weight ratio of 80/20 at various radiation doses.

### 3.2 \(T_m\) of the PLA/PBS blends

The \(T_m\) of the PLA/PBS blends at 100/0, 80/20 and 0/100 at various radiation doses were observed using DSC as seen in Table 1. It was noticed that the \(T_m\) of the pure PLA was 155°C which was higher than that of the pure PBS at 115°C. The results were in correspondence with those of previous report [4]. The value of PLA/PBS blend at 80/20 was 154°C which was slightly lower than that of the pure PLA. After irradiated, the \(T_m\) of the PLA/PBS blends tended to decrease with an increase radiation doses as a result of molecular crosslinking or molecular chain scissoring leading to a less order-packed of the polymer chain.

**Table 1.** \(T_m\) of the PLA/PBS blends at various radiation doses.

| PLA/PBS at various weight ratios | 0 kGy | 50 kGy | 100 kGy | 150 kGy |
|---------------------------------|-------|--------|---------|---------|
| 100/0                           | 155   | 154    | 151     | 149     |
| 80/20                           | 154   | 153    | 150     | 148     |
| 0/100                           | 115   | 111    | 111     | 111     |

### 3.3 Mechanical properties of the PLA/PBS blends

Flexural test of PLA/PBS blends was carried out to systematically investigate effects of radiation doses on mechanical properties of the blends as shown in figure 2.

**Figure 2.** Mechanical properties of PLA/PBS blends at different blending weight ratios: (●) 100/0, (■) 80/20 and (▲) 0/100 after irradiated at various radiation doses: a) flexural strength and b) flexural modulus.
It was found from figure 2a) that an un-radiated PLA showed flexural strength value of 187 MPa which was higher than an un-radiated PBS having the value of 116 MPa while the strength of the PLA/PBS at weight ratio of 80/20 was 129 MPa. However, the values of the PLA/PBS blends at 100/0 and 80/20 significantly decreased after radiated at 50, 100 and 150 kGy. Interestingly, the PLA/PBS at 0/100 showed a slight reduction in the flexural strength value. A higher radiation dose resulted in a reduction in flexural strength of the PLA/PBS due to some degradation degree of the blends.

From figure 2b) it was observed that the flexural modulus of the specimens was improved with radiation dose at 50 kGy which might be due to the greatest degree of crosslinking. However, the modulus value of the samples decreased with increasing radiation doses. It was attributed to the degradation of the PLA/PBS blend after radiated.

3.4 Biodegradability of the PLA/PBS blends

The biodegradation tests of the PLA/PBS at various weight ratios and different radiation doses were carried out for 28 days as illustrated in figure 3. In comparison at the same radiation doses, the PLA/PBS blend at 100/0 exhibited the greatest weight loss followed by the PLA/PBS blends at 80/20 and 0/100, respectively. After irradiated at 50 kGy, it was found that the weight loss of the specimen tended to decrease. At higher radiation doses than 50 kGy i.e. 100 and 150 kGy, the weight loss of the samples increased. The results were in accordance with the flexural modulus results i.e. the PLA/PBS after irradiated at 50 kGy showed the greatest modulus value among the others. It might because this radiation dose provided the highest degree of crosslinking while the degradation took place at radiation doses higher than 50 kGy.

4. Conclusions

The effects of the PLA/PBS blending weight ratios and radiation doses on chemical, mechanical, thermal and biological properties of the PLA/PBS blends were investigated in this research. The FTIR spectra indicated some structural change at different radiation doses. The melting temperatures of the PLA/PBS blends were decreased with increasing radiation doses. The results from flexural test revealed that the flexural strength of the specimens decreased with greater radiation doses. Interestingly, the PLA/PBS at 80/20 after radiated at 50 kGy showed the greatest flexural modulus value resulting in the lowest weight loss after biodegradation test.

5. References
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