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# Effects of electron beam irradiation on the gel fraction, thermal and mechanical properties of poly(butylene succinate) crosslinked by multi-functional monomer

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ABSTRACT

In the present work, a multi-functional monomer triallyl isocyanurate (TAIC) of 4 wt.% is incorporated into neat poly(butylene succinate) (PBS) by twin screw extrusion technique and the PBS sheets are irradiated at various electron beam absorption doses. It has been found that electron beam irradiation at an appropriate absorption dose plays an effective role in crosslinking the PBS molecules in the presence of TAIC. As a result, the irradiation influences the gel fraction, glass transition temperature, thermal stability, thermo-dimensional stability, dynamic storage modulus, and tensile properties of PBS, depending on the electron beam absorption dose applied. The improvement of the thermal and mechanical properties of PBS is most significant in the range of 50 to 70 kGy. The results are consistent with each other, supporting the electron beam irradiation effect on the property improvement of PBS.



## 1. Introduction

Bioplastics such as poly(butylene succinate) (PBS), poly(lactic acid) (PLA), and poly(ε-caprolactone), which may replace part of petroleum-based synthetic polymers, are environmentally-benign and biodegradable. Recently, bioplastics have been increasingly interested in industrial applications as well as in academic researches [1–3]. Moreover, for the past years a large number of studies on composites reinforced with natural fibers have focused on such biodegradable polymer resins as matrix [4–6].

PBS, which is thermoplastic aliphatic polyester, exhibits excellent biodegradability in nature. In our earlier studies, PBS has been frequently used as matrix resin of a biocomposite system with silk fibers due to its good processability and toughness [7–9]. PBS can also be processed in films, fibers, or pellets. PBS has poor mechanical and thermal properties. Hence, the property improvement of neat PBS is often needed for extended applications. There are two main approaches to improve the mechanical and thermal properties of biodegradable polymers such as PLA and PBS. One approach is by incorporating a multi-functional monomer of appropriate concentration into a targeting polymer, and then by crosslinking the polymeric molecules by electron beam irradiation [10–12]. The other approach is by reinforcing the biodegradable matrix with natural fibers or with other reinforcements [13–16].

everal papers have been dealing with crosslinking of PLA in the presence of multi-functional monomer by means of electron beam technique [10,11,17,18]. However, a few studies have been performed on the radiation effect on the crosslinking of PBS prepared by plastomilling or hot-pressing [19,20]. As electron beam irradiates to a polymer, either crosslinking or chain scission of polymer molecules can occur competitively depending on the electron beam energy as well as on the polymer type [21,22]. In the case of electron beam crosslinking, a multi-functional monomer plays a significant role in chemically bridging between the polymer chains. Multi-functional monomers such as triallyl isocyanurate (TAIC), trimethylallyl isocyanurate (TMAIC), and trimethylallyl isocyanurate (TMPTA), which can generate free radicals by electron beam, may be used for crosslinking. It has been reported that among them TAIC is the most effective to increase the mechanical properties of biodegradable polymers through the electron beam crosslinking [10,11,23].

Suhartini et al. reported the radiation crosslinking of PBS in the presence of trimethallyl isocyanurate [19] and also they used low electron beam energy of 20 kGy only for gelation of PBS [24]. Bahari et al. reported the radiation crosslinked PBS foam with blowing agents and the biodegradation up to 400 kGy [20]. No papers have dealt with PBS with TAIC produced by twin screw extrusion processing and subsequently crosslinked by electron beam energy of about 50 kGy. Consequently, the objectives

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of the present study are primarily to produce PBS pellets containing a multi-functional monomer TAIC through compounding and twin-screw extrusion processes and ultimately to investigate the effect of the electron beam irradiation (10 to 150 kGy) on the gel fraction, glass transition temperature, melting temperature, thermal stability, thermo-dimensional stability, dynamic mechanical property, and tensile property of TAIC-containing PBS, in comparison with those of neat PBS.

## 2. Material and methods

### 2.1. Materials

PBS pellets (Model G4560-J) used in this work were supplied by S-EnPol Inc., Korea. According to the manufacturer's information, the glass transition temperature is about −35 °C, the crystallization temperature is in the range of 90–100 °C, and the melting temperature is about 115 °C. The 'as-supplied' neat PBS pellets were dried at 80 °C for 5 h in a convection oven in order to avoid possible moisture absorption prior to compounding and extrusion processes. TAIC (96% purity) purchased from TCI Co., Japan was used as a multi-functional monomer for crosslinking PBS molecules by means of electron beam irradiation. TAIC is in liquid state and it has the molecular weight of 249. The freezing point and the boiling point are 24 °C and 140 °C, respectively. Fig. 1 shows the chemical structures of PBS and TAIC.

### 2.2. Preparation of TAIC-containing PBS pellets and sheets

A modular intermeshing co-rotating twin-screw extruder (BT-30-S2-421, LG Machine Co., Korea) with the screw diameter of 30 mm and the L/D ratio of 42 was used for compounding neat PBS pellets with TAIC and for producing TAIC-containing PBS pellets, as seen in Fig. 2. Prior to compounding neat PBS with TAIC, PBS pellets and TAIC were placed in a polyethylene bag together, and well mixed by a manual shaking manner. The concentration of TAIC in the PBS/TAIC mixture was 4 wt.%. The mixture was cooled down to −18 °C for 3 h. Here, −18 °C was lower than the freezing point of TAIC. Use of −18 °C was to solidify the TAIC in neat PBS pellets, to feed the PBS/TAIC mixture uniformly into the extruder hopper, and also to carry out the compounding efficiently. The reason for using 4 wt.% TAIC is that the boiling point of TAIC is much lower than the maximum extrusion processing temperature of 180 °C used in the present work. Consequently, although 4 wt.% TAIC was inputted to the neat PBS, about 3.3 wt.% TAIC was finally remained in the PBS compound due to partial removal of TAIC occurring during the extrusion process. It has been reported earlier [11,18,23] that in the presence of 3.0 to 3.5 wt.% TAIC results in the best crosslinking efficiency of PLA molecules.

Three kneading disk block configurations were used to obtain efficient melting and compounding of neat PBS with TAIC. Barrel temperatures were set to 90, 100, 110, 120, 130, and 140 °C, respectively, increasing the temperature from the feeder to the die of the extruder. The screw speed was 100 rpm and the extruding speed was 5 kg/h. The PBS/TAIC extrudate was continuously cooled down to ambient temperature using water, and then cut to 2–3 mm in average length using a pelletizer. The PLA/TAIC pellets were dried 80 °C for 5 h in a convection oven prior to fabrication of PBS sheets. The PBS sheets were prepared from the TAIC-containing PBS pellets by using a hot-pressing method, as illustrated in Fig. 2. The holding time for 2 min at 150 °C was applied. A pressure of 1000 psi (6.89 MPa) was applied. A number of PBS sheets with the thickness of 300–320 μm were fabricated repeatedly.

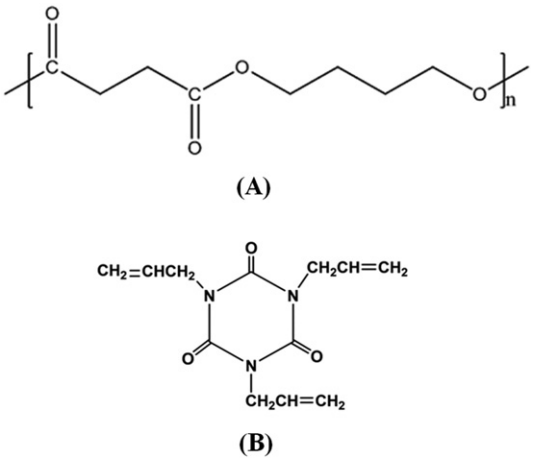


**Fig. 1.** Chemical structures of poly(butylene succinate) (A) and triallyl isocyanurate (B).

### 2.3. Electron beam irradiation

Electron beam irradiation of PBS sheets was carried out using an electron beam apparatus (ELV-8, EB Tech Co., Korea), as shown in Fig. 2. The process was performed with 2.5 MeV and 9.8 mA at ambient temperature in air. A few PBS sheets were placed on top of a conveyor cart for irradiation. Various electron beam absorption doses of 10, 30, 50, 70, 100 and 150 kGy were applied. The individual absorption doses were applied to each sample by counting the rotation number of the conveyor cart passing through the channel equipped with electron beam irradiation facility in the middle of the channel. The conveying speed was 10 m/min throughout the irradiation process. The experimental layout of electron beam irradiation is described in detail elsewhere [18].

### 2.4. Characterization

#### 2.4.1. Gel fraction measurement

The gel fraction of neat PBS and TAIC-containing PBS sheets irradiated at various electron beam absorption doses was measured by comparing the weight change of the specimens before and after being immersed in excessive chloroform for 24 h. After the immersion, soluble PBS, which was not crosslinked, was removed using a filter paper with the diameter of 150 mm and the pore size of 5 μm. After removing the chloroform remaining on the specimen surfaces, the gel fraction of unirradiated and irradiated specimens was calculated by using the following equation.

$$\text{Gel fraction}\ (\%) = w_2/w_1 \times 100$$

where $w_1$ and $w_2$ are the weight of the PBS specimens (gels) measured before and after the immersion test, which were not dissolved in isopropanol, respectively.

#### 2.4.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA Q500, TA Instruments, USA) was performed with the sample of 10–15 mg to investigate the thermal stability and degradation behavior of neat PBS and TAIC-containing PBS pellets. The heating rate of 20 °C/min was used purging a nitrogen gas. A can-type alumina pan with the depth of 10 mm was used. Derivative thermogravimetry (DTG) curves were also obtained to examine the weight loss rate as a function of temperature.

#### 2.4.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC 200F3 maia, NETZSCH Co., Germany) was performed from −60 to 150 °C purging a nitrogen gas to examine the change of the glass transition temperature and melting temperature of PBS sheets. The heating rate was 10 °C/min. The sample of about 10 mg in an aluminum pan was used for the measurement.

#### 2.4.4. Thermal expansion measurement

Thermomechanical analysis (TMA 2940, TA Instruments, USA) was carried out to 100 °C with the heating rate of 10 °C/min purging a nitrogen gas to examine the thermal expansion behavior of PBS sheets