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RADIATION CROSSLINKING OF BIODEGRADABLE POLY(BUTYLENE SUCCINATE) AT HIGH TEMPERATURE

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ABSTRACT

Poly(butylene succinate), (PBS) with different molecular weight was γ-irradiated at different temperatures and various doses. PBS with high molecular weight and smaller peak area of crystal melting gave the highest gel content at the same temperatures and dose. A two-step irradiation (irradiation in molten state after irradiation at room temperature) gave the highest gel content in different conditions. This is due to the formation of network structure by pre-irradiation at room temperature that leads to less degradation. PBS prepared by two step irradiation was effective for improvement of heat stability because of high gel content formation. Unirradiated PBS sheets broke immediately at 110°, while the irradiated sample (gel fraction, 50%) by a two step-method, did not break even up to 200 minutes at 130°C. The PBS sheets are biodegradable even after crosslinking.

Key Words: Poly(butylene succinate)(Bionolle); Radiation crosslinking; Heat resistability; Biodegradation; Molten state.

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INTRODUCTION

Waste disposal has become a serious problem worldwide because solid waste made up of plastic materials continues to increase. Environmental concerns generated by plastic materials are generating interest toward the development of ecological products. Accordingly, many kinds of biodegradable plastic materials have been developed [1]. Current commercial biodegradable polymers are predominantly limited to aliphatic polyesters, polyethers, poly(vinyl alcohol) and polysaccharides. Among these, the synthetic biodegradable polymers are more important. Aliphatic polyesters such as polylactic acid (PLA), polyglycolic acid (PGA), poly(lactide-co-glycolide) (PLG) are widely used for parenteral drug delivery systems [2]. Poly(ε-caprolactone) (PCL) has been used for plastics packaging and plant containers [3]. Poly(hydroxy butyrate) (PHB) has been reported to produce a biodegradable foam [4]. Aliphatic polyesters are one of the most promising materials for biodegradable fibers and films. Biological degradation is the decomposition of a polymer under natural environmental conditions. Biodegradable polymers are converted to carbon dioxide and water when they come in contact with soil that contains microorganisms.

Poly(butylene succinate) (PBS), trade name Bionolle, is produced through the polycondensation reaction of glycols such as ethylene glycol and butanediol-1,4 and aliphatic dicarboxylic acids such as succinic acid and adipic acid used as principal raw materials. The polymer is available in various grades (Table 1) [5].

The application of biodegradable polymers is limited either for economical reasons or for difficulties related to their processing, often due to their poor thermal stability. Irradiation is one of the methods used to improve certain properties of polymers by crosslinking or grafting, and it also is a more environmentally friendly process since no chemical initiator is needed. It has been reported that heat stability, deformation resistance, solvent resistance of wire and cable have been improved by irradiation crosslinking [6]. PCL irradiated by gamma rays from a ^{60}Co source in the super-cooled state led to the higher gel content and has high heat stability [7]. Hot water resistance of PVA sheets was also improved by radiation crosslinking [8]. When epoxy-based compositions were irradiated, they acquire high thermal resistance, excellent water, and oil resistance. So far, the enzyme method, the microorganism method, and the soil burial method have been used to evaluate the biodegradability of polymer materials [9].

Table 1. Properties of PBS Used in This Work

PBS	M_w	DSC, ΔH(J/g)	Melting Point (°C)	MFR (g/10min)
1	1.08×10^5	46	91	1
2	7.36×10^4	70	112	5
3	6.35×10^4	81	114	29

In the present work, crosslinking behavior and heat resistance of crosslinked PBS in various phases have been investigated. Enzymatic degradation and a soil burial test were also carried out to evaluate their biodegradability.

EXPERIMENTAL

Materials

Three kinds PBS produced at Showa High Polymer Co. Ltd., Japan were used in this work. The properties of various PBS are listed in Table 1. These polymers were dried in a vacuum oven at 50°C for 48 hours before use. The enzyme (Lipase AK) was purchased from Amano Co. Ltd., Japan for an enzymatic test.

Sheet Preparation

40 g sample pellets were kneaded using a Toyoseiki Labo Plastomill Mixer (Model 50C150) at 120°C for 10 minutes. Sheets for irradiation of the kneaded samples were prepared by preheating at 120°C for 6 minutes using a 0.5 mm spacer, and pressing for 3 minutes at the pressure of 150 kg/cm^2 in a hot press. Then the sheets were cooled to room temperature at the pressure of 100 kg/cm^2 using water as a coolant in a cold press. The sheets were cut into dumbbell shaped pieces.

Irradiation of the Samples

Sample pellets or sheets were sealed in a vacuum (10^{-3} torr) glass tube. Then, the samples were irradiated by gamma rays from a ^{60}Co source with a dose rate of 10 kGy/h at different temperatures using an apparatus for controlling temperature.

Analytical Measurements

Molecular weight was measured by GPC (HLC-802A, Tosoh Co., Ltd., Japan). The fluent was chloroform with a flow rate of 1 ml/min and the polymer concentration was 1 mg/ml. The average molecular weights were calibrated using polystyrene standards.

Melting temperatures were measured using Differential Scanning Calorimeter (Perkin-Elmer DSC-7) under a nitrogen flow of 30 ml/min with a heating rate of 10°C/min.

MFR was measured using a Melt Flow Indexer (Toyoseiki Co. Ltd.) at 190°C.

Heat Stability

Heat stability of irradiated samples was measured using an oven at different temperatures. The irradiated dumbbell shaped pieces of (0.3 × 2) cm^2 area and 0.05 cm thickness were hung in an oven with a given load at various temperatures. The times to break the pieces were recorded.

Measurement of Gel Fraction

The irradiated samples were extracted by using refluxing chloroform for 48 hours. The samples were dried at room temperature after extraction and then kept in a vacuum oven at 50°C to a constant weight. Gel fraction was determined according to the following equation

$$\text{Sol fraction (s)} = (W_0 - W_1)/W_0 \quad (1)$$

$$\text{Gel fraction (\%)} = (1 - s) \times 100\% \quad (2)$$

where W_0 and W_1 are weight of sample before and after extraction, respectively.

Biodegradation Test

The enzymatic degradation and soil burial tests were carried out by determining the samples weight loss of (irradiated and unirradiated) after the enzymatic reaction and soil burial.

A enzymatic test method of has been reported by Iwamoto [10]. The samples with a dimension of 10 mm × 10 mm × 0.12 mm were dried in a vacuum oven for 20 hours at 50°C. Then the samples were put into test tubes that contain a reaction solution (1) 4.0 ml 0.2 M phosphate buffer, pH 7.0 (2) 1.0 ml 0.1% $MgCl_2$ surfactant (3) 1.0 ml (10 mg) enzyme, Lipase AK, and incubated at 50°C with shaking for various periods. After a certain period of incubation, the samples were taken out and washed with distilled water and methanol, then dried in a vacuum oven to constant a weight at 50°C to calculate the samples weight loss.

The soil burial test was carried out in plastic troughs containing 1/3 rusty soil and 2/3 black garden soil. The dumbbell shaped pieces (irradiated and unirradiated) with a thickness of 0.5 mm were buried about 3 cm below the soil surface so that the oxygen supply is sufficient, for different a burial time from 1 to 4 months. The samples were taken out from the soil, cleaned using running water, and dried in an oven at 50°C to a constant weight.

The samples weight loss after the enzymatic reaction and soil burial test was calculated using the following equation:

$$\text{Weight loss (\%)} = (W_0 - W_1)/W_0 \times 100\% \quad (3)$$

where W_0 and W_1 are the sample weight before and after the enzymatic reaction or soil burial, respectively.

RESULTS AND DISCUSSION

Crosslinking at Various Temperatures

Figure 1 shows the gel fraction of three kinds of PBS samples against the irradiation dose at room temperature. The gel fractions of PBS1 and PBS2 increase with an increasing dose. However, PBS3 did not produce gel even at 210 kGy. Figure 2 shows the gel fraction of three kinds of PBS samples at various temperatures for the dose of 210 kGy. The gel fractions of three kinds of PBS samples increase gradually with increasing the temperature, and at a temperature more than the melting point, it is a remarkable increase. The relationship between gel fraction and irradiation dose at a molten state is shown in Figure 3. PBS1 gave the highest gel content among the three kinds of PBS samples at the same temperature and same dose. The crosslinking reactions predominantly depend on the chemical structure and morphology, especially crystallinity and molecular weight of polymer. PBS1 has a lower melting point and a lower area of crystal melting (ΔH) compared to those of other two samples and has a higher molecular weight. Since radiation crosslinking takes place in the amorphous area of the polymer, PBS1 gave the highest crosslinking among the three PBS. The higher molecular weight

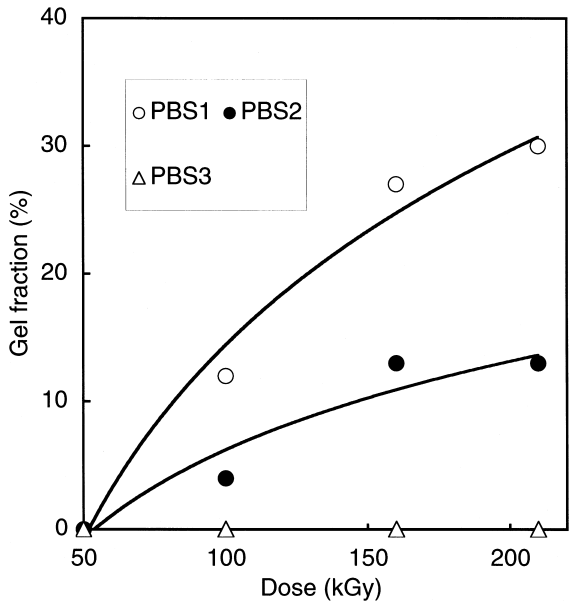

Figure 1. Gel fraction against dose for various PBS at room temperature in vacuum.

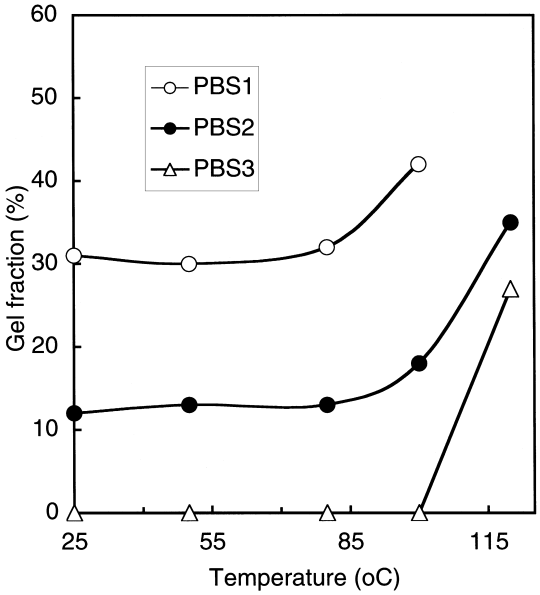

Figure 2. Gel fraction of PBS irradiated with a dose of 210 kGy at different temperature in vacuum.

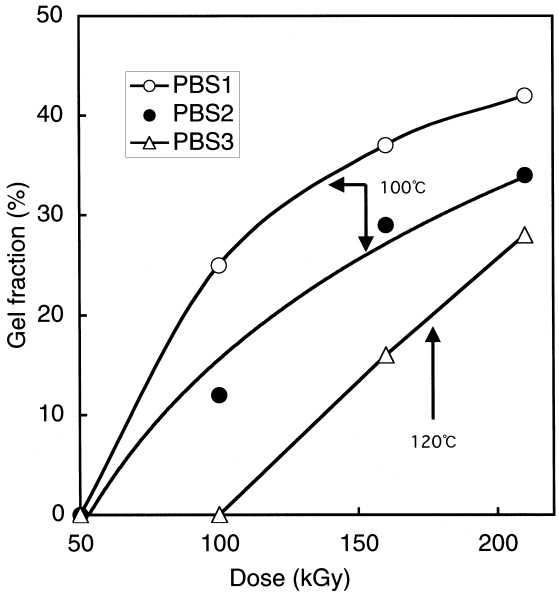

Figure 3. Gel fraction against dose at molten state in vacuum.

polyethylene has a higher gel fraction, since it has a high probability of producing a crosslinking site in one molecule and polymer twinning [6].

Two-Step Irradiation of PBS1

Figure 4 shows the gel fraction of PBS1 in a two-step irradiation that is irradiation at a molten state after irradiation at room temperature. From previous results, it is found that irradiation at a molten state (100°C) gave a higher gel content compared to that of irradiation at room temperature. Hence, PBS1 was irradiated at 100°C after irradiation for 160 kGy at room temperature. The gel content reached 58%, which is 17% higher compared to the molten state for 210 kGy in direct irradiation (one step irradiation). The physical state of the polymer, such as amorphous, crystalline, vitreous, highly elastic or viscous state depends on the temperature. When polyethylene was irradiated at a high temperature or molten state, it produced a higher gel fraction than that of irradiation at room temperature. When the temperature was raised to the molten state (100°C), it gave an increased amorphous content leading to higher polymer chain mobility for radicals recombination than that of room temperature. So raising the temperature usually leads to an increase in radiation crosslinking rate. The crosslinking of polymer materials occurs by recombination reaction of radicals formed by irradiation. The network structure formed by pre-irradiation at room temperature leads to less degradation,

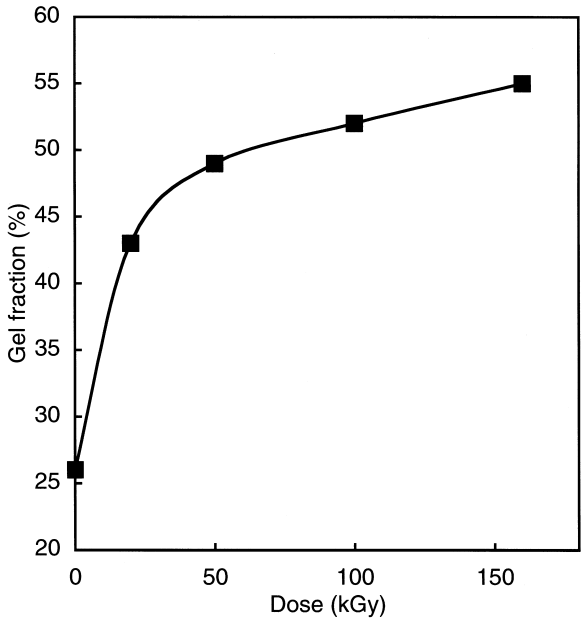

Figure 4. Gel fraction of PBS1 irradiated at molten state after irradiation with a dose of 160 kGy at room temperature.

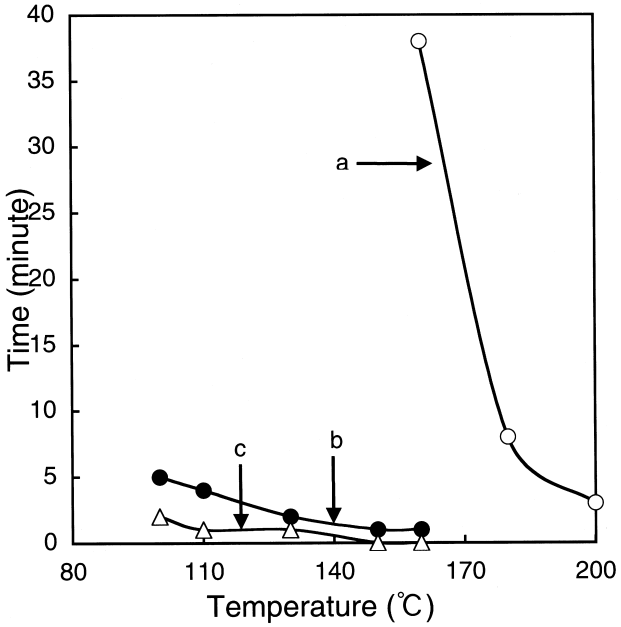

Figure 5. Relationship between temperature and breaking time of PBS1 with applied stress of 6.67 kgf/cm^2. (a) Gel fraction, 50% (Irradiation at 100°C for 50 kGy after irradiation at room temperature for 160 kGy); (b) Gel fraction, 33% (Irradiation at 80°C for 210 kGy); (c) Unirradiated sample.

thus irradiation of PBS at 100°C after irradiation for 160 kGy at room temperature gave the highest gel content in the different irradiation doses.

Heat Resistance of Crosslinked PBS1

Heat resistance of irradiated PBS1 was tested by measuring the breaking time of sheets at different temperatures. The sheets were kept at different temperatures with a constant stress (0.667 MPa) in an oven. The results are shown in Figure 5. Unirradiated PBS1 sheets broke immediately at 110°C, while for two steps irradiated sample (gel fraction, 50%) gave very high heat stability. At 130°C, it did not break even up to 200 minutes and at 180°C for 8.3 minutes.

Biodegradation Test

The enzymatic degradation test of the unirradiated and irradiated PBS1 samples is shown in Figure 6. The unirradiated sample shows a higher degradation rate compared to the irradiated one. This is because the irradiated PBS1 sample contains a three-dimensional network formed during irradiation. The crosslinked network retards the reaction with an enzyme. A similar result has been reported in the degradation of γ-rays irradiated PCL samples using the same enzyme [11].

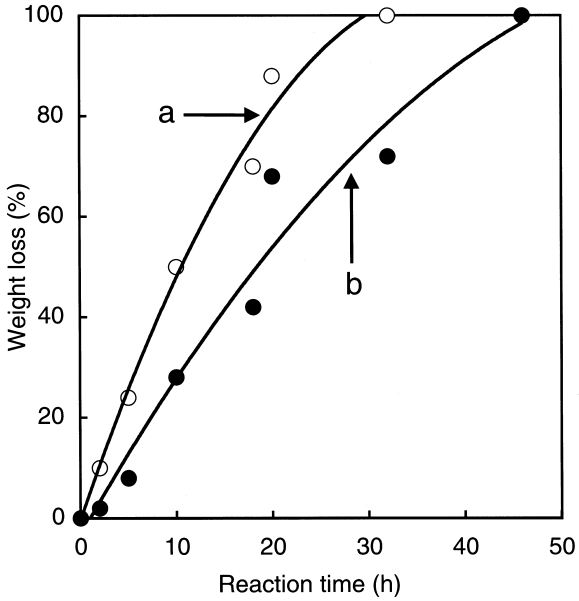

Figure 6. Weight loss in enzymatic degradation of PBS1. (a)Unirradiated sample; (b) Irradiation at 100°C for 50 kGy after irradiation at room temperature for 160 kGy. Gel fraction, 50%. Reaction temperature 50°C; Enzyme concentration, 1.67 mg/ml; Sample thickness, 0.12 mm.

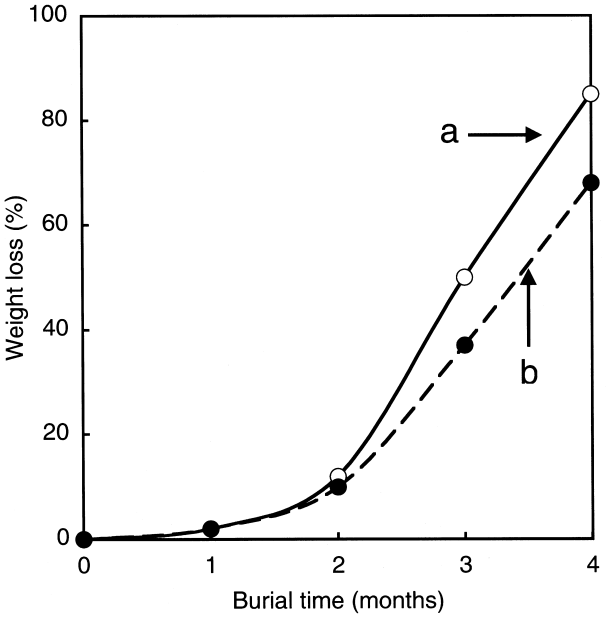

Figure 7. Soil burial degradation of PBS1. Sample thickness, 0.5 mm. (a) Unirradiated sample; (b) Irradiation at 100°C for 50 kGy after irradiation at room temperature for 160 kGy. Gel fraction, 50%.

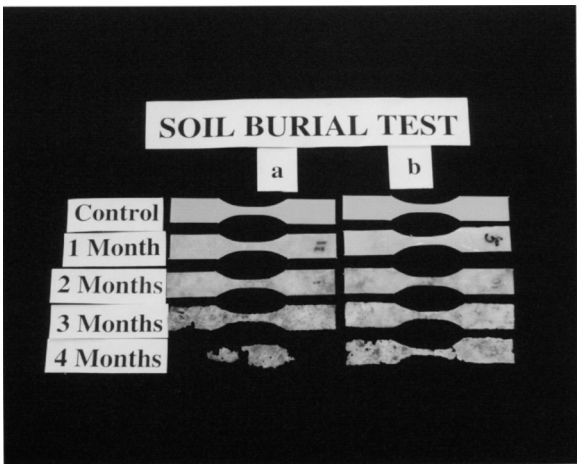

Figure 8. Photograph of PBS1 after buried in soil for different periods. (1) control; (2) after 3 months; (3) after 4 months; (a) unirradiated PBS1; (b) Irradiation at 100°C for 50 kGy after irradiation at room temperature for 160 kGy.

There was a 49% weight loss of an unirradiated sample after a 10 hour immersion, while there was a 28% weight loss for the irradiated sample. The unirradiated sample was completely decomposed after 32 hours, however a weight loss of 73% was observed for the irradiated sample. The film sample was not destroyed, but became thinner. This is because the degradation first takes place on the polymer surface by contacting with the enzyme, then gradually goes to the inside. Enzymatic degradation in PBS1 easily occurs, even a crosslinking structure is introduced by irradiation.

The result of soil burial degradation of the uncrosslinked and crosslinked samples is shown in Figure 7. It is seen that for uncrosslinked and crosslinked samples, the weight loss gradually increases with an increased burial time up to 4 months. However, a weight loss of the crosslinked samples is equal to th uncrosslinked ones in the first two months. This is probably due to several factors such as temperature, pH, humidity and oxygen availability, which may affect the results. With increasing the burial time, the weight loss of unirradiated samples is higher than that of the irradiated ones. This is due to that irradiated samples contain the crosslinking network formed during irradiation. After 4 months' burial time, a weight loss of 86% was achieved for the uncrosslinked sample, while for the crosslinked samples (gel content 50%), weight loss of 69% was achieved. A photograph of PBS1 after burial in soil for different periods are shown in Figure 8.

CONCLUSION

Irradiation crosslinking of PBS1 without any additive at a molten state after irradiation at room temperature gave a higher gel content than other conditions.

Moreover, the crosslinked PBS1 had a higher heat resistance and higher biodegradability.

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