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1. INTRODUCTION

Poly(3-hydroxybutyrate) [P(3HB)] and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)] are microbial biodegradable polyesters produced by many types of bacteria (1). Poly(butylene succinate) (PBS) and poly(ϵ -caprolactone) (PCL) are also biodegradable synthetic polyesters which have been commercialized. These thermoplastics are expected for wide usage in environmental protection and biocompatible applications (2).

Radiation grafting of hydrophilic monomers onto many polymers, e.g., polyethylene (3) and polypropylene (4, 5) has been studied mainly for biomedical applications.

In the present study, radiation-induced graft polymerization of vinyl monomers onto PHB and P(3HB-co-3HV) was carried out and improvement of their properties was studied. Changes in the properties and biodegradability were compared with the degree of grafting. Radiation-induced crosslinking of PBS and PCL which relatively show thermal and irradiation stability was also carried out to improve their thermal stability or processability. Irradiation to PBS and PCL mainly resulted in crosslinking and characterization of these crosslinked polyesters was investigated.

2. EXPERIMENTAL

Materials and radiation-induced graft polymerization

P(3HB) and P(3HB-co-3HV) containing 24 % 3HV, which were isolated from *Alcaligenes eutrophus*, were purchased from Aldrich Chemical Co. Styrene (St) monomer was mainly used though methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AAc) monomers were used for comparison. P(3HB) or P(3HB-co-3HV) sample was pre-irradiated with ⁶⁰Co γ -rays (dose rate, 5 kGy/h) at -78°C under reduced pressure (10^{-3} torr). After irradiation, vinyl monomer was introduced to the irradiated polymers under vacuum. Then the reaction was carried out at a desired temperature for various periods of time (called post-polymerization). After grafting, the samples were Soxhlet extracted with solvents for 3 days and dried under vacuum to constant weight.

Degree of grafting X_g (%) was determined by the percent increase of weight based on the initial sample weight W_i (g), using equation:

$$X_g = [(W_g - W_i) / W_i] \times 100 \quad (1)$$

where W_g (g) is the weight of sample after grafting.

Materials and radiation-induced crosslinking

PCL sample was purchased from Daicel Chemical Co. Ltd., Japan (PCL-H7). PCL pellets sealed in a glass tube were irradiated using ^{60}Co γ -rays with a dose rate of 10 kGy/h under a controlled temperature in vacuum or air conditions. Gel fraction was measured as remaining weight ratio after completely extracted with the solvent to the initial sample weight.

PBS samples were purchased from Showa High Polymer Co. Ltd., Japan (Bionolle). To make a foam, two blowing agents, azodicarbonamide compound (BX81) which release a N_2 gas, and sodium carbonate compound (V-20N) which on heating release a CO_2 gas supplied by Mitsubishi Chemical Co. Ltd. were used.

Bionolle pellets were blended with blowing agents at 135°C for 5 min using plastomill, and sheets of 0.5 mm thick were prepared at 135°C for another 3 min by a hot press. Then they were irradiated in air with 2 MeV accelerator at various doses (a dose of 10 kGy/pass). In order to produce a foam, the irradiated sheet was heated by hot press at 200°C using spacer of 3 mm for 1 min.

Analytical procedures

Melting point T_m and glass transition temperature T_g were measured with a Perkin Elmer Model DSC-7 differential scanning calorimeter (DSC) at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. The melting peak temperature was calibrated with high-purity standards.

Gel permeation chromatography (GPC) was carried out with a liquid chromatograph HLC-802A (Tosoh Co. Ltd) at 38°C . The eluent was chloroform with a flow rate of 1 ml/min. The molecular weights were calibrated using polystyrene standards.

Enzymatic degradation

The enzymatic degradation of P(3HB) and its copolymer by the PHB depolymerase purified from *A. faecalis* T1 was carried out at 37°C in 0.1 M phosphate buffer (pH 7.4) with shaking. The films (initial weights, 11-13 mg, film dimensions, $10 \times 10 \times 0.1$ mm) were immersed with 1 ml of the buffer. The reaction was started by the addition 32 μl of an aqueous solution of PHB depolymerase (8 μg). Weight loss of the film (X_d) was calculated by the percent decrease of weight based on the initial film weight W_i (g), using equation,

$$X_d = [(W_i - W_d) / W_i] \times 100 \quad (2)$$

where W_d (g) is the weight of sample after the enzymatic degradation.

Enzymatic degradation of PBS and PCL by lipase AK enzyme (purchased from Amano pharmaceutical Industry Co. Ltd., Japan) was carried out in 0.2 M phosphate buffer (pH 7.0). The films were put into reaction mixtures (6.0 ml buffer, 10 mg of lipase AK, and 0.1% surfactant) and incubated at 55°C with shaking for various periods of time.

3. RESULTS AND DISCUSSION

Radiation-induced graft polymerization of P(3HB) and P(3HB-co-3HV)

Fig. 1 shows the effect of temperature on the grafting of St onto P(3HB) at pre-irradiation dose of 5 kGy. The X_g was increased with increasing temperature and the grafting at 80°C was the largest X_g , 25% for reaction time of 4 h. Whereas grafting of St onto the copolymer, the X_g at 50°C was the largest among these reaction temperatures. Graft polymerization of polymers such as polyethylene (6) and polypropylene (7) occur in amorphous part when radical formed in crystalline regions migrated to interface of the crystal. The copolymer has lower crystallinity than P(3HB) so that molecular mobility is more active than that of P(3HB).

Fig. 2 shows number average molecular weight

M_n of graft PSt against reaction time at 70°C at pre-irradiation dose of 15 kGy. The grafted P(3HB) was treated with 20% aqueous methylamine to remove completely the trunk polymer P(3HB) and the graft PSt was isolated. The M_n of branched PSt for P(3HB) is increased largely up to 1 h in grafting and the increment of M_n ceases for 3 h. This result corresponds to grafting behaviors Fig. 1. Hence it is suggested that increase of X_g in grafting time is due to increase of molecular weight of branch PSt since longer PSt chain has formed. Moreover, M_n of branched PSt for P(3HB) reduced remarkably up to 10 kGy and it is almost similar at dose of 15 kGy. It shows that at higher dose many grafting points are created but M_n is lower due to the formation of short PSt chain. Accordingly, X_g of preirradiation dose of 15 kGy is 1.6 times higher than that of 10 kGy pre-irradiation, or in other words, the number of branch PSt chain is 1.6 times larger in the former.

Fig. 3 shows enzymatic degradation profiles of P(3HB) and P(3HB-co-24% 3HV) graft-polymerized with MMA, HEMA and AAc. MMA

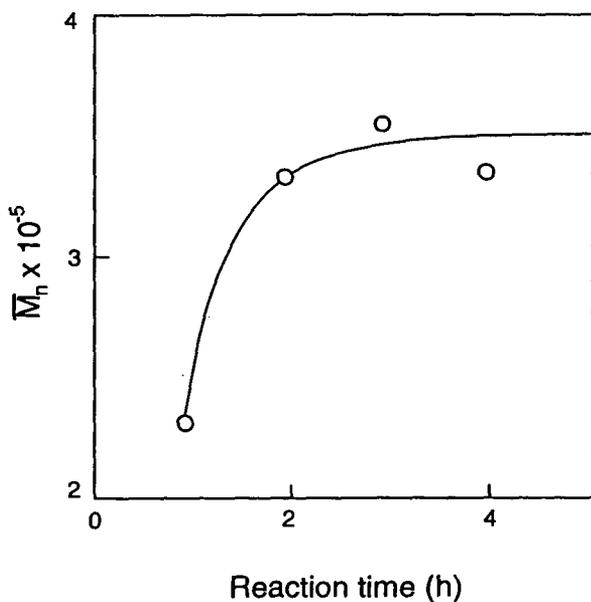


Fig. 2. M_n of graft PSt against reaction time

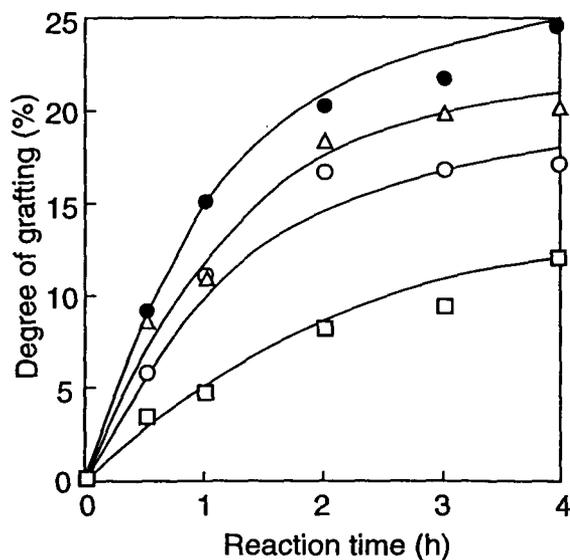


Fig. 1. Effect of temperature on St grafting onto P(3HB) at pre-irradiation dose of 5 kGy

□ 30°C; ○ 50°C; △ 70°C; ● 80°C

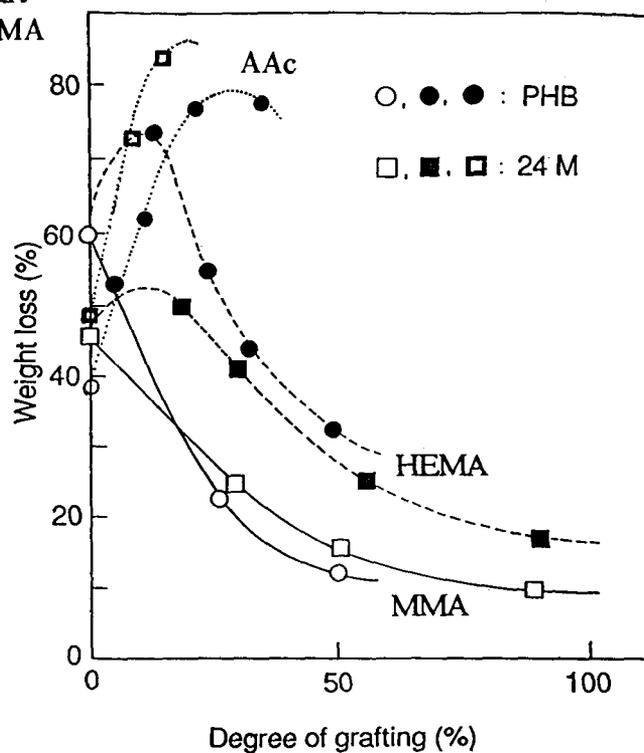


Fig. 3. Enzymatic degradation of P(3HB) and P(3HB-co-24% 3HV) graft-polymerized with MMA, HEMA and AAc

grafted samples show steep decrease in weight loss (8), whose behavior is similar to St grafted samples, while HEMA grafted samples show maximum weight loss at 15 % of X_g , and AAc grafted samples show maximum weight loss at 20-30 % of X_g . The AAc grafted samples show the highest weight loss (9). This promotion is due to improvement of wettability of the polymer and the enzymatic solution.

Foam formation of Bionolle (PBS) by irradiation

The effect of blowing agent on crosslinking is shown in Fig. 4. BX81 of 5% was added into Bionolle and BX81 gives 10% higher gel fraction than pure Bionolle. St/EVA contained in BX81 compound disperse blowing materials such as azodicarbonamide homogeneously in Bionolle during kneading and St/EVA have same tendency as that of Bionolle blended with BX81 compound. Since EVA is a radiation crosslinking type, BX81 compound promote crosslinking of Bionolle. Bionolle blends of 5% BX81 having relatively lower gel fraction irradiated with dose of 100-150 kGy is preferred to produce suitable foams (10).

Fig. 5 shows enzymatic degradation of Bionolle foam and Bionolle samples. The weight loss of the foam is steeply increased up 48 h and then leveled off to about 24% at 96 h. This value is four times larger than that of the irradiated Bionolle after 96 h. Significant increase in surface area of the foamed sample causes promotion of enzymatic degradation. The morphologies of foam having a large number of cell structure, as the cell expand, some cell walls become very thin like membrane and allow to erode easier than the unfoamed Bionolle. The weight loss of unirradiated Bionolle is higher than the irradiated Bionolle. This is because the irradiated Bionolle contain the crosslinked part that retards the erosion.

Radiation-induced crosslinking of PCL

Fig. 6 shows gel fraction of PCL irradiated in the solid state (at room temperature), in the molten state or in the supercooled state under vacuum. Irradiation in molten state (80°C) results in higher gel content compared to room temperature (27°C). At room temperature, PCL contains crystalline regions where crosslinking is hardly formed. At

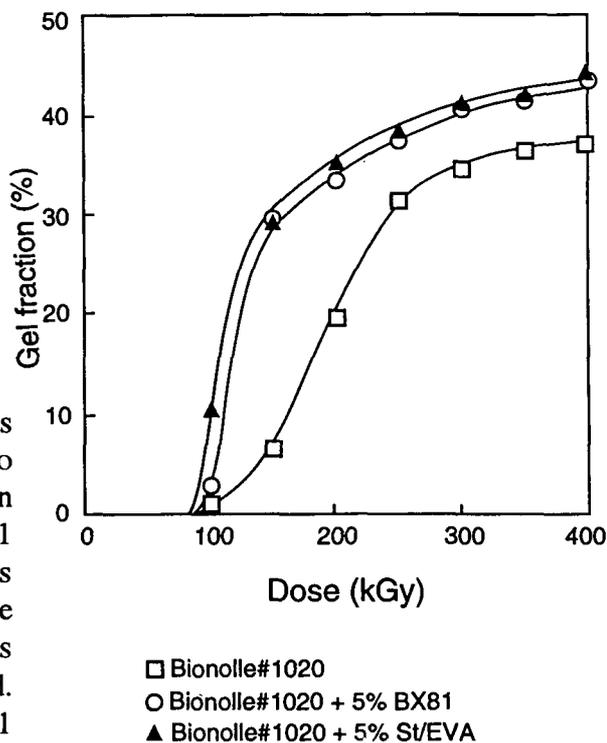


Fig. 4. Gel fraction of Bionolle, that blended with BX81 or St/EVA against irradiation dose

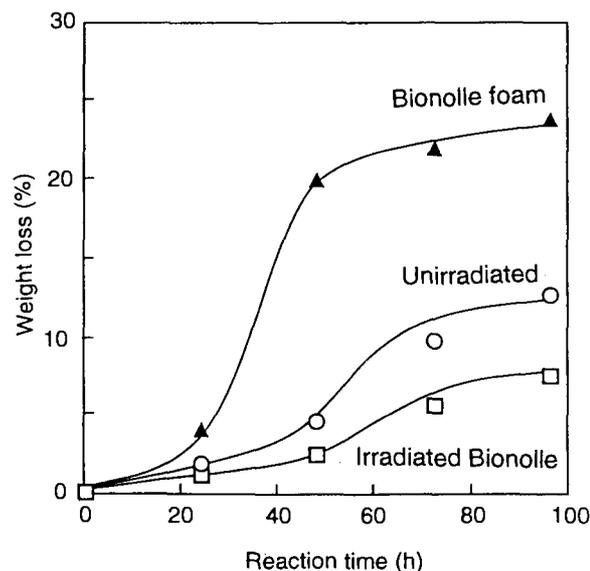


Fig. 5. Enzymatic degradation of Bionolle foam and Bionolle sample at 55°C

80°C, PCL is converted to completely amorphous state. However, during irradiation voids are formed in the polymer due to the gases evolved, which cause a reduction in various physical properties. In order to avoid the formation of voids, PCL was irradiated at 35°C to 55°C after melting. Irradiation of PCL at 45°C or lower results in free of voids gel, while irradiation at 50°C and 55°C produces gels which contain many voids as shown in Fig. 7. As shown in Fig. 7, PCL obtained by irradiation in the supercooled state has a homogeneous shape without voids, and sheets hot-pressed from this crosslinked PCL showed transparent appearance or low haze value (11).

Enzymatic degradation of PCL with different gel fractions obtained by irradiation is shown in Fig. 8. One hundred percent of gel was obtained by removal of the sol fraction of irradiated sample at 160 kGy. It can be seen that the enzymatic degradation reduces almost linearly as gel fraction increases, however the degradation still occurred even at 100% of gel fraction.

Improvement of processability of PCL by radiation techniques

Molecular weight or shapes of PCL irradiated with the dose below 30 kGy changed significantly. Fig. 9 shows MFR curves of PCL irradiated under vacuum and air atmospheres. MFR was estimated by measuring weight of samples flowed for 10 minutes from extrusion machine (Toyoseiki Co. Ltd., Japan). It can be seen that MFR reduces remarkably up to 20 kGy and followed by steady decreases with further increase of dose. Irradiation under vacuum gives lower value compared to that

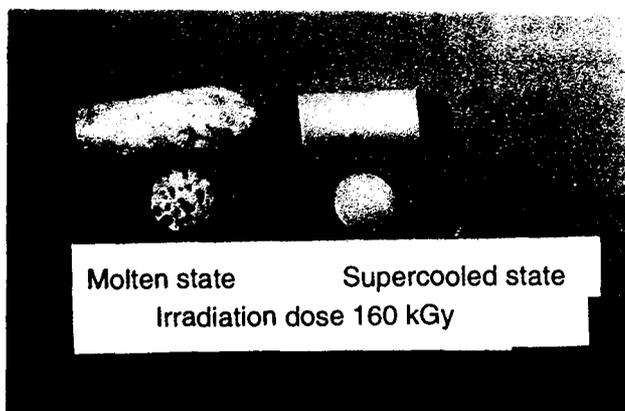


Fig. 7. Photographs of irradiated PCL

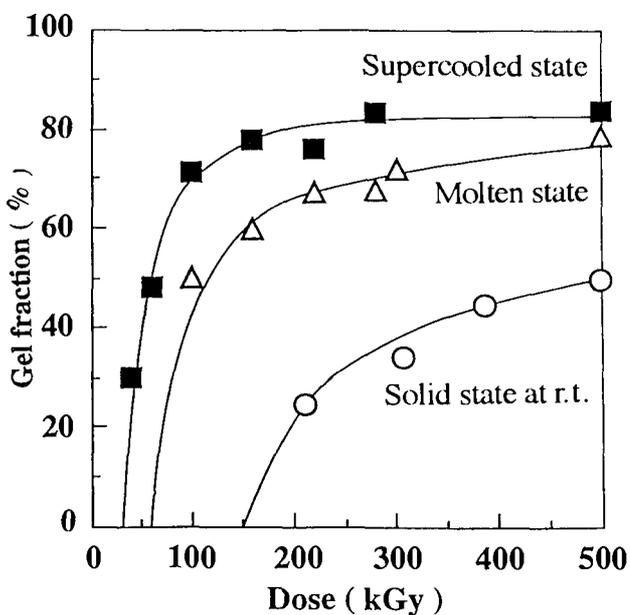


Fig. 6. Gel fraction of PCL irradiated in solid, molten and supercooled states under vacuum

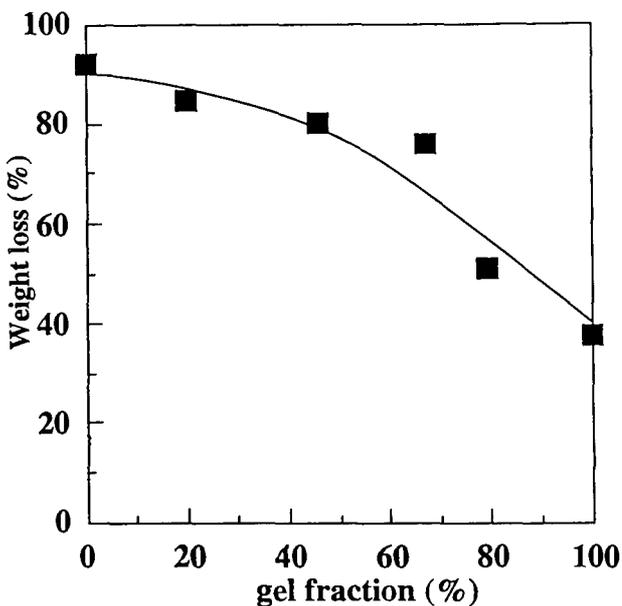


Fig. 8. Enzymatic degradation of PCL with different gel fraction obtained by irradiation

in air at the same dose.

Table I shows average molecular weights of irradiated PCL. M_n and polydispersity of PCL increased by introducing crosslinking between molecular chains.

Fig. 10 is dynamic modulus of PCL at various irradiation doses against temperature. Unirradiated PCL easily flows above 70°C, while PCL irradiated with dose of 30 kGy shows a wide temperature range (90-210°C) of processing and PCL irradiated with 15 kGy shows an intermediate temperature range. This means PCL molecules change into partially crosslinked or non-linear shape, e.g., star shape.

Table I. Molecular weights of irradiated PCL

Dose (kGy)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	\bar{M}_w/\bar{M}_n
0	9.26	16.25	1.75
15	13.55	27.54	2.03
30	12.56	34.07	2.71

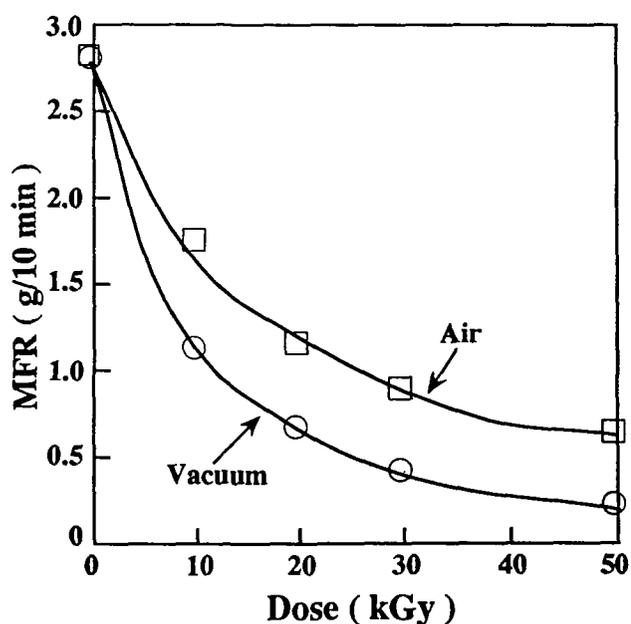


Fig. 9. MFR curves of PCL irradiated under vacuum and air atmospheres

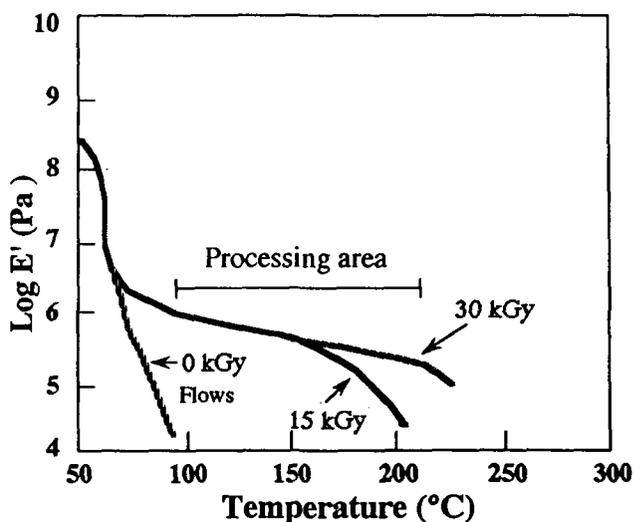


Fig. 10. Dynamic modulus of PCL at various irradiation doses against temperature

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