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Biodegradability of poly(3-hydroxybutyrate) film grafted with vinyl acetate: Effect of grafting and saponification

Yuki Wada[a,*], Noriaki Seko[b], Naotsugu Nagasawa[b], Masao Tamada[b], Ken-ichi Kasuya[a], Hiroshi Mitomo[a]

[a]Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan
[b]Environment and Industrial Materials Research Division, Quantum Beam Science Directorate, Japan Atomic Energy Agency, 1233 Watanuki-machi, Takasaki, Gunma 370-1292, Japan

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Abstract

Radiation-induced graft polymerization of vinyl acetate (VAc) onto poly(3-hydroxybutyrate) (PHB) film was carried out. At a degree of grafting higher than 5%, the grafted films (PHB-g-VAc) completely lost the enzymatic degradability that is characteristic of PHB due to the grafted VAc covering the surface of the PHB film. However, the biodegradability of the PHB-g-VAc films was recovered when the films were saponified in alkali solution under optimum conditions. Graft chains of the PHB-g-VAc film reacted selectively to become biodegradable polyvinyl alcohol (PVA). The biodegradability of the saponified PHB-g-VAc film increased rapidly with time.

Keywords: Poly(3-hydroxybutyrate); Radiation grafting; Enzymatic degradation; Saponification; Poly(vinyl acetate); Poly(vinyl alcohol)

1. Introduction

Bacterial poly(3-hydroxybutyrate) (PHB), a well-known biodegradable thermoplastic polyester (Saito and Doi, 1994), has many advantages including biodegradability and biocompatibility. However, the practical application of PHB has been restricted by its brittleness and stiffness, and the enzymatic degradability of PHB must be controlled in order to enable utilization.

Recently, our research group has succeeded in controlling the enzymatic degradability of PHB using the radiation graft copolymerization method (Mitomo et al., 1995; Mitomo et al., 1996; Bahari et al., 1997; Bahari et al., 1998; Cakmakli et al., 2001). Acrylic acid (AAc) (Mitomo et al., 1996), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) (Mitomo et al., 1995), and styrene (St) (Bahari et al., 1997; Bahari et al., 1998; Cakmakli et al., 2001) were grafted onto PHB resulting in a significant decrease of enzymatic degradability of PHB grafted with MMA, whereas the enzymatic degradability of PHB was increased by the introduction of hydrophilic HEMA. From these results, it was concluded that the biodegradability of grafted PHB would be affected by hydrophilicity of the grafted polymers. This method of changing the enzymatic degradability by grafting proved to be very effective. However, it was disadvantaged by the fact that the graft chains remained without being degraded.

PVA, which is produced by saponification of poly(vinyl acetate) (PVAc), is a biodegradable polymer. In our previous study, graft polymerization of VAc to PHB was carried out, and the difference in enzymatic degradability of PHB-g-VAc before and after saponification in methanol including NaOH was investigated. As a result, the enzymatic degradability of saponified PHB-g-VAc was observed to increase. However, when the grafted PHB were saponified in alkali solution, there was the possibility not only of saponification of PVAc as graft chains, but also of degradation of the PHB substrate. Therefore, it was difficult to determine the effect of saponified graft chains from measuring the enzymatic degradability. In the present study, first, the effect of grafting with VAc on PHB was

*Corresponding author. Tel.: +81 27 346 9394; fax: +81 27 346 9381.
E-mail address: wada.yuki@jaea.go.jp (Y. Wada).

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reviewed. Then pre-irradiation graft polymerization of VAc onto PHB films was carried out. The enzymatic degradability of PHB-g-VAc films and saponified PHB-g-VAc films, optimal conditions of saponification, and the thermal properties and biochemical oxygen demand (BOD) degradability of PHB-g-VAc films were also investigated.

2. Experimental

2.1. Materials

Microbial PHB was purchased from Aldrich Chemical Co. Ltd. The PHB was purified as follows: PHB was dissolved in chloroform, then poured into a mixed solvent of *n*-hexane and methanol (1:1 vol%). The precipitated PHB powder was filtered and dried in vacuum.

The purified PHB powder was preheated to produce PHB film at 190 °C for 3 min, which was then hot-pressed at 190 °C for 5 min. The obtained films with a size of 150 mm × 150 mm × 150 μm were cooled using a cold press for 5 min. The PHB films were crystallized isothermally at 90 °C for a week before use. A VAc monomer purchased from Kanto Chemical Inc. was used without further purification. Nonion L-4 as the surfactant was supplied by NOF Corporation and used directly.

2.2. Preparation of PHB powder and film grafted with VAc

2.2.1. Preparation of PHB powder grafted with VAc

PHB-g-VAc powders were prepared using techniques of pre-irradiation of radiation-induced graft polymerization. PHB powder (0.5 g) was placed into one side of an H-shaped glass ampoule sealed under reduced pressure (10^{-3} Torr). The PHB was then pre-irradiated with ^{60}Co γ-rays (dose rate, 10 kGy/h) at 10 kGy in the glass ampoule at −70 °C. After irradiation, the VAc monomer (3.0 mL) was poured from the opposite side of the ampoule. The air was evacuated by a vacuum line and the ampoule was sealed under reduced pressure (10^{-3} Torr). The grafting reaction was carried out in a temperature-controlled water bath at 60 °C for 1 h before the PHB and PHB-g-VAc powders were immersed in methanol to stop the grafting reaction. These powders were soxhlet-extracted with acetone at 85 °C for 72 h to remove the residues of VAc monomer and homopolymers.

2.2.2. Preparation of PHB film grafted with VAc

The PHB films were cut into 10 × 60 mm pieces, packed into polyethylene bags in a nitrogen atmosphere, and irradiated with electron beams of 2 MeV and 3 mA. The irradiation dose was set at 10 kGy. The irradiated PHB films were placed into a glass reactor. After a vacuum was formed, the films were contacted with various mixture solutions of VAc emulsion solution (Mesquita et al., 2004; Gomez-Cisneros et al., 2005) with a 10:1 (w/w) ratio of VAc and surfactant (Nonion L-4) for 0.5, 1, and 2 h. The reaction temperature was maintained at 60 °C by dipping the glass reactors in a warm bath. After the grafting reaction, the grafted PHB films were immersed in methanol for 1 h at 60 °C to remove residues of both VAc monomer and homopolymers.

The degree of grafting (X_g) was calculated from the following equation (Basuki et al., 2003):

$$X_g(\%) = (W_g - W_0) \times 100/W_0,$$

where W_0 and W_g are the weights of PHB films before and after graft-polymerization, respectively.

2.3. Saponification conditions of PHB-g-VAc powder and films

2.3.1. Saponification conditions of PHB-g-VAc powder

Saponification reaction of PHB-g-VAc powders (0.5 g) was carried out in a beaker for 30 min at 25 °C. After addition of 0.05 M of NaOH with the methanol in the beaker, this solution including PHB-g-VAc powders was stirred so that uniform saponification took place. After saponification, the product was washed with methanol, filtered with the Rohto, and dried under reduced pressure at room temperature.

2.3.2. Saponification conditions of PHB-g-VAc films

For PHB-g-VAc films, saponification temperature (10, 25, and 40 °C), saponification time (1, 2, 4, and 8 h), and concentration of NaOH were changed to investigate optimum saponification conditions. The saponification reaction of PHB-g-VAc films (10 mm × 10 mm, 5 pieces) was carried out in a beaker containing methanol (100 mL) and 0.02, 0.05, and 0.1 M of NaOH for a predetermined time.

The degree of saponification (D_s) was calculated from following equation:

$$D_s(\%) = (W_g - W_s)/(W_{gc} \times 44/86) \times 100,$$

where W_g and W_s are the weights of PHB-g-VAc films before and after saponification, respectively. W_{gc} is the weight of graft chains in the grafted films and $W_{gc} \times 44/86$ indicates the ideal value at which the graft chains completely become biodegradable PVA before degradation of the PHB substrate (Xie et al., 1998).

2.4. Characterization of PHB-g-VAc films

2.4.1. Enzymatic degradability of PHB-g-VAc powder and films

The enzymatic degradation of PHB-g-VAc powders and films was determined in a 0.1 M phosphate buffer (pH 7.4) at 37 °C. PHB depolymerase purified from *Ralstonia pickettii* T1was used for enzymatic degradation (Feng et al., 2004).

2.4.1.1. Enzymatic degradability of PHB-g-VAc powder before and after saponification. PHB-g-VAc powders (0.2 g) and saponified PHB-g-VAc powders (0.2 g) were