

Synthesis and Photo- and Biodegradabilities of Poly[(hydroxybutyrate-co-hydroxyvalerate)-g-phenyl vinyl ketone]

JIN PARK, JONG-GU PARK, WON-MOON CHOI, CHANG-SIK HA, WON-JEI CHO

Department of Polymer Science & Engineering, Pusan National University, Pusan 609-735, Korea

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ABSTRACT: The graft copolymer, poly[(hydroxybutyrate-co-hydroxyvalerate)-g-phenyl vinyl ketone] [P(HBV-g-PVK)], was synthesized by graft polymerization of phenyl vinyl ketone (PVK) onto poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) under nitrogen atmosphere using benzoyl peroxide. The structure of P(HBV-g-PVK) was identified by Fourier transform IR and $^1\text{H-NMR}$ spectra. The effects of weight ratio of PVK to PHBV in feed, initiator concentration, reaction time, and reaction temperature on the grafting ratio and grafting efficiency were investigated. The thermal decomposition temperature of P(HBV-g-PVK) was 272°C. The tensile strengths of P(HBV-g-PVK) after photo- or biodegradation were significantly decreased due to degradation by UV irradiation or *Aspergillus niger*. The value of color difference (ΔE) of P(HBV-g-PVK) was greater than that of PHBV. The film surfaces of P(HBV-g-PVK) treated with UV irradiation and *Aspergillus niger* showed many pits as compared with the untreated P(HBV-g-PVK). It has been found that the photo- and biodegradabilities of P(HBV-g-PVK) was excellent. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1432–1439, 1999

Key words: photo- and biodegradable polymer; graft polymerization; poly[(3-hydroxybutyrate-co-hydroxyvalerate)-g-phenyl vinyl ketone]; UV irradiation; color difference; *Aspergillus niger*

INTRODUCTION

The photo- and/or biodegradable polymers are attracting much interest from the theoretical and practical standpoints.^{1–4} Among biodegradable polymers, poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) have been studied for their syntheses, properties, and applications, because they exhibit higher biodegradability and biocompatibility, and lower toxicity than conventional synthetic polyesters such

as polypivalolactone and polyethylene terephthalate.^{5,6} The photodegradable polymers containing the oxygen moiety such as hydroperoxide, peroxide, and carbonyl groups have also been the main subject of numerous investigations.^{7–13} It was known that one of the most useful methods to obtain the photodegradable polymer is to incorporate the carbonyl group, which is able to absorb UV light in a polymer.¹⁴

The aim of this work was to synthesize new photo- and biodegradable graft polymers containing carbonyl and PHBV moieties, because many graft polymers have been synthesized to improve properties in our laboratory.^{15–23} In this study poly[(hydroxybutyrate-co-hydroxyvalerate)-g-phenyl vinyl ketone] [P(HBV-g-PVK)] was synthesized by graft copolymerization of phenyl vinyl ketone (PVK) onto PHBV under nitrogen atmo-

Correspondence to: W.-J. Cho.

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Table I Graft Copolymerization Conditions Used in This Study

Condition	Description
Weight ratio of Phenyl vinyl ketone to PHBV	1, 2, 3, 4
Initiator concentration (wt %) ^a	1, 2, 3, 4
Reaction time (h)	24, 36, 48, 72
Reaction Temperature (°C)	50, 60, 70, 80

^a Weight ratio of BPO was based on 10 g of PHBV.

sphere by using benzoyl peroxide (BPO). The effects of weight ratio of PVK to PHBV in feed, initiator concentration, reaction time, and reaction temperature were studied on the graft polymerizations. The structure and thermal decomposition of the synthesized P(HBV-g-PVK) were examined. The photo- and biodegradabilities of P(HBV-g-PVK) were evaluated by Fade-o-Meter and by *Aspergillus niger*, respectively. The tensile strength and morphology of P(HBV-g-PVK) before and after photo- and biodegradations were also investigated.

EXPERIMENTAL

Materials

PHBV (Aldrich Chemical Co.; PHV content: 5 wt %) was used as received. Phenyl vinyl ketone (Aldrich Chemical Co.) was purified according to the procedure described in the literature.²⁴ BPO (Hayashi Chemical Co., Japan) was recrystallized from methanol. 1,2-Dichloroethane, methyl ethyl ketone (MEK), and benzene were distilled prior to use.

Graft Polymerization of PVK onto PHBV

A given amount of PHBV was dissolved in 150 mL of 1,2-dichloroethane and the solution was poured into a three-neck round bottom flask with different weight ratio of BPO as an initiator under nitrogen atmosphere, and then the PVK monomer was added to the PHBV solution. The reaction was carried out under various experimental conditions as shown in Table I. After a chosen period of polymerization, the contents were poured into excess methanol with stirring; the precipitate was filtered by using the 1G3 glass filter and dried in a vacuum oven until kept at a constant weight. As shown in Figure 1, the formed poly(phenyl vinyl ketone) (PPVK) and nongrafted PHBV in the

products were removed by extraction with MEK and benzene for 24 h by Soxhlet apparatus, respectively. Finally, the benzene solution of the synthesized P(HBV-g-PVK) was precipitated in excess methanol and dried in a vacuum oven until kept at a constant weight. The grafting ratio and grafting efficiency were estimated as the following equations^{25,26}:

Grafting ratio (%) =

$$\frac{\text{weight of polymer in grafts}}{\text{weight of substance}} \times 100 \quad (1)$$

Grafting efficiency (%) =

$$\frac{\text{Weight of polymer in grafts}}{\text{Total weight of polymer formed}} \times 100 \quad (2)$$

Measurements

Thermal Decomposition Temperature

Thermal decomposition temperature of the graft copolymers was examined with a Dupont 951 TGA instrument under N₂ atmosphere at a scanning rate of 10°C/min.

Tensile Strength

The tensile strength was measured using a Universal Testing Machine (Hounsfield M-series

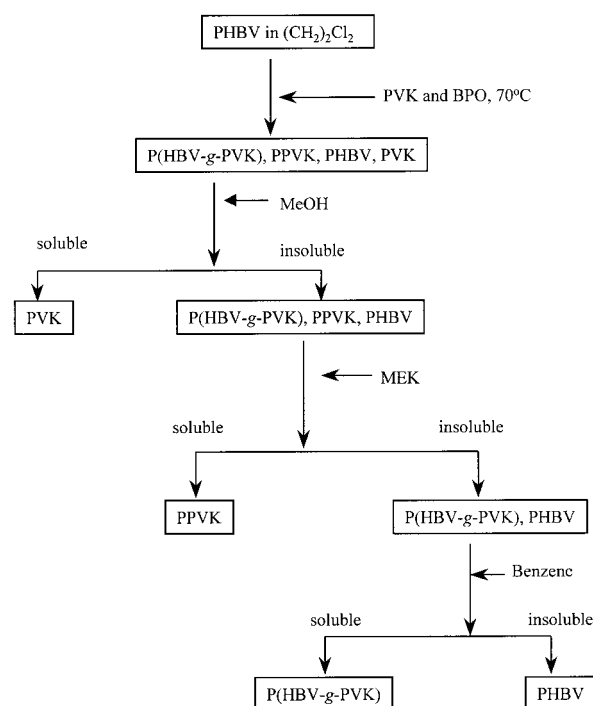


Figure 1 Isolation process for P(HBV-g-PVK).

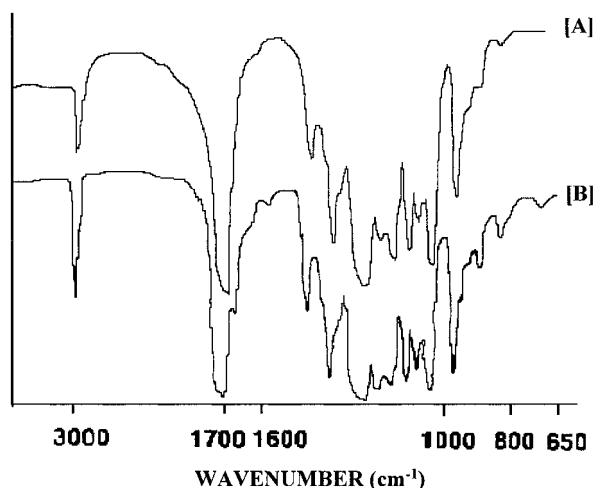


Figure 2 IR spectra of PHBV (A) and P(HBV-g-PVK) (B).

500L). The test specimens were prepared according to the procedure of ASTM D638-84. The cross-head speed was 5 mm/min and the initial gauge length was adjusted at 25 mm.

Morphology

The micrographs of the samples before and after photo- and biodegradations were obtained by a scanning electron microscopy (SEM) instrument [JEOL JSM35-CF], respectively.

After biodegradation, the sample cultured with *A. niger* was gently washed with methanol in order to remove the free debris and air dried. The samples were coated by platinum prior to placing in the SEM chamber.

Photodegradability²⁷⁻²⁹

The photodegradabilities of samples exposed to UV irradiation using Fade-o-Meter (Atlas, at 60°C and 65% relative humidity) were determined by a color difference meter (ND-101 DP). The prepared film specimens were cast from 1,2-dichloroethane solution (ca. 3 wt %) on a nonyellowing urethane-coated hiding paper. The films were slowly dried at room temperature and then dried under vacuum until kept a constant weight. The cross-sectional area of the films was $5 \times 10 \text{ cm}^2$, with a thickness of 35 μm . The color difference value (ΔE) of the films after exposure to UV light was calculated using the Hunter-Schöfield equation.³⁰

Biodegradability³¹

The *A. niger* (KCTC 2118) was used as a fungus, cultured in potato dextrus agar slant at 30°C for 48 h, and stored at 4°C and then the incubated fungus was cultured on the graft copolymer films to evaluate the biodegradability. Media used for the biodegradation were as follows: culture medium consisted of NaNO_3 (3.0 g), K_2HPO_4 (1.0 g),

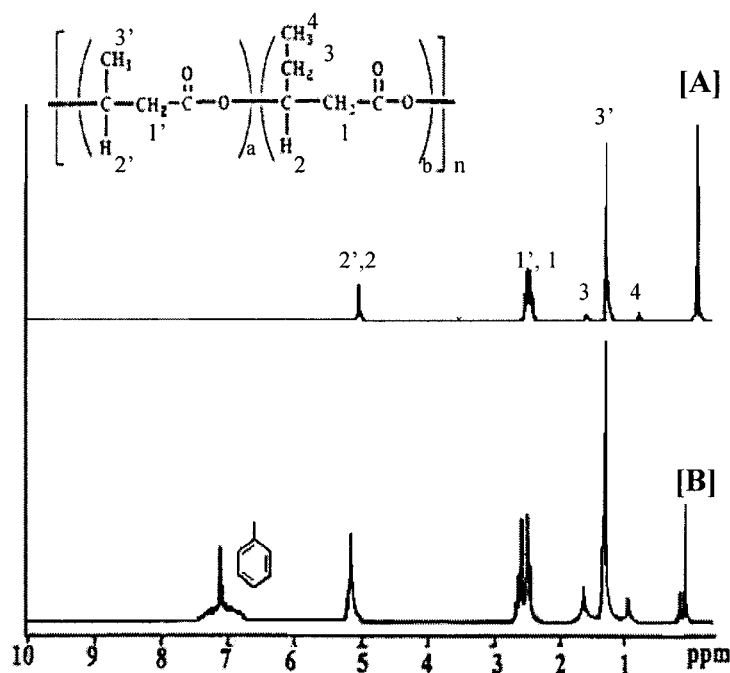


Figure 3 ^1H -NMR spectra of PHBV (A) and P(HBV-g-PVK) (B) (in CDCl_3).

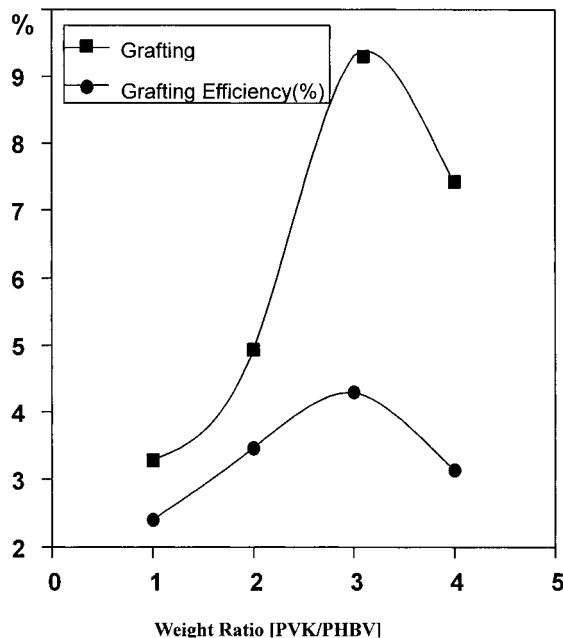


Figure 4 Effects of weight ratio of PVK to PHBV in feed on the graft copolymerization: reaction temperature, 70°C; reaction time, 48 h; BPO, 2 wt % (based on PHBV).

MgSO₄ 7H₂O (0.5 g), KCl (0.5 g), FeSO₄ 7H₂O (0.01 g), sucrose (30 g), and agar (15 g) per liter distilled water.

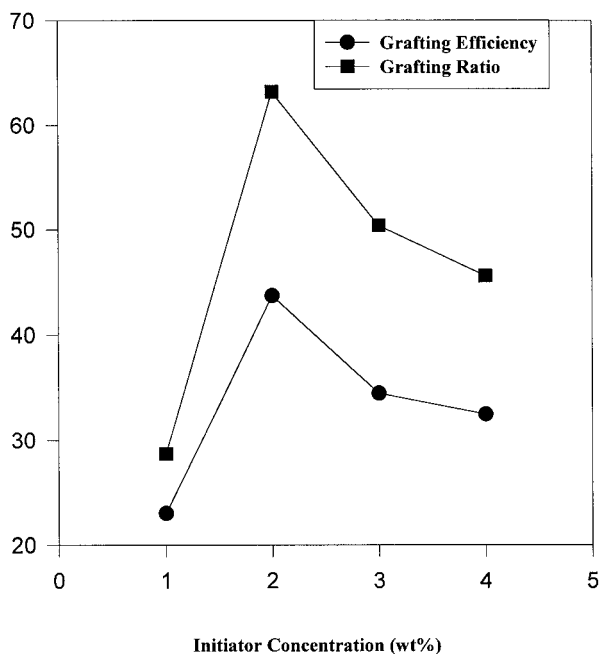


Figure 5 Effects of initiator concentration on the graft copolymerization: [PVK]/[PHBV] = 2.0; reaction temperature, 70°C; reaction time, 48 h.

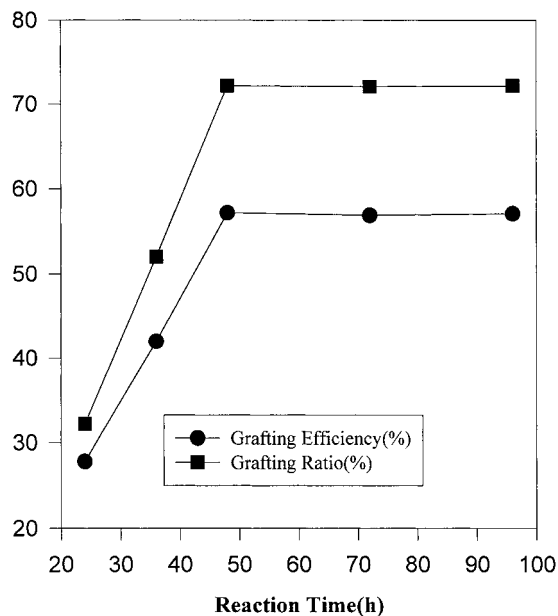


Figure 6 Effects of reaction time on the graft copolymerization: [PVK]/[PHBV] = 2.0; reaction temperature, 70°C; BPO, 2 wt % (based on PHBV).

RESULTS AND DISCUSSION

Characterization

The structure of the synthesized P(HBV-g-PVK) was identified by Jasco FT/IR-5300 spectrophotometer. As shown in Figure 2, several characteristic peaks in the IR spectrum of P(HBV-g-PVK) appeared at 1726 and 1684 cm⁻¹ (C=O: stretching vibration in PHBV and PPVK unit), 1597 cm⁻¹ (C=C bond; stretching vibration of phenyl group in PPVK unit), and 704 cm⁻¹ (aromatic =C-H; out-of-plane vibration), respectively. The ¹H-nmr (FT-300 MHz Varian Gemini 2000) spectrum [Fig. 3(B)] of P(HBV-g-PVK) compared with that of PHBV [Fig. 3(A)] showed characteristic peaks of aromatic ring protons at 7.2 ppm, methine protons at 5.3 ppm, methylene protons at 2.5–2.7 ppm, and methyl protons at 2.2 ppm.

Effect of Reaction Condition

Monomer Feed Ratio

The graft copolymerizations of PVK onto PHBV were carried out with the monomer concentrations of 1–4 weight ratios in feed. From Figure 4, it can be seen that the grafting ratio and the grafting efficiency were increased with increasing weight ratio of PVK to PHBV up to 3, and thereafter they were rapidly decreased. The decreasing

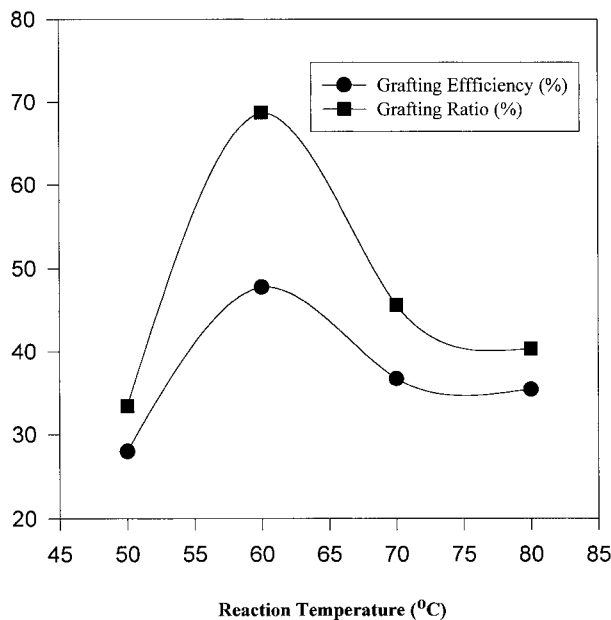


Figure 7 Effects of reaction temperature on the graft copolymerization: [PVK]/[PHBV] = 2.0; reaction time, 48 h; BPO, 2 wt % (based on PHBV).

phenomena at higher weight ratio mean that PPVK homopolymer is formed more easily than a graft polymer, P(HBV-*g*-PVK).

Initiator Concentration

The effects of initiator concentration on the graft copolymerizations are shown in Figure 5. The grafting ratio and efficiency increased with increasing initiator concentration up to 2.0 weight %, but thereafter they decreased rapidly with further increase of initiator concentration. The decrease in grafting efficiency is attributed to the reason that PPVK homopolymer was formed more readily than P(HBV-*g*-PVK) at higher initiator concentrations.

Table II Thermal Decomposition Temperature of PHBV, P(HBV-*g*-PVK), and PPVK

Samples	Ratio of PVK to PHBV ^a	Thermal Decomposition Temperature (°C)
PHBV	—	267
P(HBV- <i>g</i> -PVK)	1	264
	2	267
	3	272
	4	266
PPVK	—	352

^a Weight ratio of PHBV to PVK in feed.

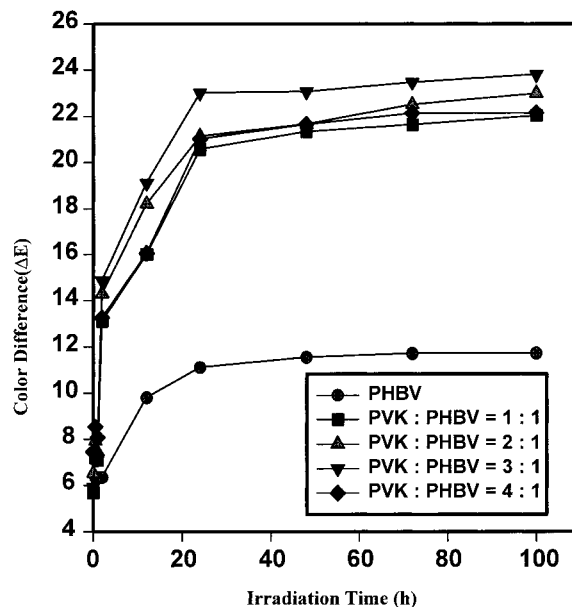


Figure 8 Plot of color difference (ΔE) versus irradiation time for PHBV and P(HBV-*g*-PVK).

On the other hand, it reveals that the formation of active radical from the reaction between initiator and PVK is easier than initiator and PHBV.

Reaction Time

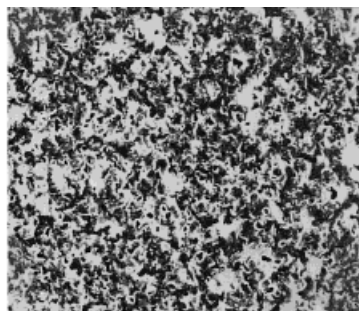
The effect of reaction time on the graft polymerization was shown in Figure 6. The weight ratio of PVK to PHBV in feed was fixed at 2.0 together with BPO of 2 weight % based on PHBV. The grafting ratio and efficiency were linearly increased with increasing reaction time up to 48 h, but thereafter they leveled off. This increasing result is attributed to that the graft polymerization occurs more easily than homopolymerization within that time. As a result, the grafting efficiency and grafting ratio are increased as predicted from eqs. (1) and (2). The phenomenon after that time may be the cause of the similar rates of formation of homopolymer and graft polymer.

Reaction Temperature

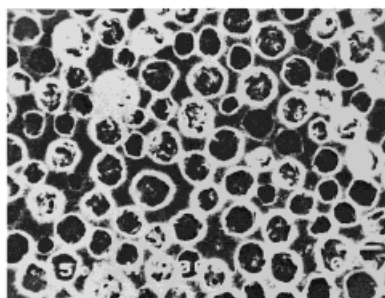
Figure 7 shows the effect of reaction temperature on the graft copolymerization. Grafting ratio and efficiency passes through a maximum at 60°C. Above this temperature, the grafting reaction decreased rapidly. This phenomenon means that the rate of homopolymerization is higher than that of graft polymerization at high temperature.

Thermal Stability

Table II shows the thermal degradation temperatures of P(HBV-*g*-PVK) prepared from the vari-



[A] Before photo- and biodegradation (x 1000).



[B] After photodegradation for 100 h with UV-irradiation (x 1000).



[C] After biodegradation for 36 days with *Aspergillus niger* (x 1000).

Figure 9 Scanning electron micrographs of P(HBV-*g*-PVK) before and after photo- and biodegradation tests ($\times 1000$).

ous weight ratios of PVK to PHBV in feed. The initial decomposition temperature of P(HBV-*g*-PVK) showed 272°C when the weight ratio of PVK to PHBV in feed was 3. The thermal degradation temperature of P(HBV-*g*-PVK) was less than that of PPVK.

Photodegradability

The photodegradation was semiquantitatively expressed in terms of color difference (ΔE) with the National Bureau of Standards Unit.³² Figure 8 shows the photodegradation effects on the weight ratios of PVK to PHBV in feed. The higher ΔE value has, the better photodegradability exhibits. In Figure 8, the ΔE values of polymers increased

with increasing UV light irradiation time up to 24 h and thereafter they leveled off. The color differences of P(HBV-*g*-PVK) were increased with increasing concentration of PVK to PHBV under UV light irradiation time up to 24 h. The color difference value of the synthesized P(HBV-*g*-PVK) was higher than that of PHBV. This result can be explained by Norrish type I or II cleavage for a polymer containing a ketone group.^{33,34} Norrish type I scission results in the formation of free radicals by the cleavage between carbonyl carbon and α -carbon. The formed radicals participate in further degradation reactions. Norrish type II scission results in the formation of an unsaturated polymer chain end and a polymer chain with

an end carbonyl group by the abstraction of a hydrogen on the γ -carbon. Thus, the degradation of poly(PHBV-*g*-PVK) can be mainly related to the PVK moiety, because the ketone group of PVK moiety in poly(PHBV-*g*-PVK) was bonded to the ethyl and phenyl group at the side chain of poly(PHBV-*g*-PVK). This explanation is consistent with the fact that carbonyl group in ketone absorbs UV light well.^{33,34}

Biodegradability

The P(HBV-*g*-PVK) film was treated with *A. niger* for 36 days at 30°C. The surface of film was covered with *A. niger*. The film surface after biodegradation showed remarkably many pits on its micrograph due to biodegradable PHBV moiety in P(HBV-*g*-PVK) as compared with before biodegradation.

Morphology

After exposure under UV irradiation for 100 h, the morphologies of P(HBV-*g*-PVK) were investigated by scanning electron microscopy. As shown in Figure 9(B), P(HBV-*g*-PVK) showed many pits as compared with untreated P(HBV-*g*-PVK) [Fig. 9(A)]. Therefore it is shown that the P(HBV-*g*-PVK) film has excellent susceptibility to UV light. This may be attributed to the photodegradable PVK moiety^{33,34} in P(HBV-*g*-PVK). The surface of the P(HBV-*g*-PVK) film after incubation for 36 days was investigated by SEM. The film surface of P(HBV-*g*-PVK) [Fig. 9(C)] showed extensive grooves and many pits due to biodegradation property of PHBV moiety in P(HBV-*g*-PVK) as compared with film before incubation [Fig. 9(A)]. Thus it is believed that P(HBV-*g*-PVK) film has excellent photo- and biodegradabilities.

Tensile Strength

The tensile strengths of the samples before and after photo- or biodegradation are shown in Figure 10. The tensile strength values of P(HBV-*g*-PVK) after irradiation for 100 h were decreased as compared with untreated P(HBV-*g*-PVK). After biodegradation for 36 days, the tensile strength of P(HBV-*g*-PVK) was also decreased due to the attack of *A. niger*, which proves the biodegradability of the polymers. The tensile strength of P(HBV-*g*-PVK) after photodegradation was lower as compared to that after biodegradation. The tensile strength of P(HBV-*g*-PVK) that was undertook UV light irradiation was larger than that of PHBV treated by the same condition.

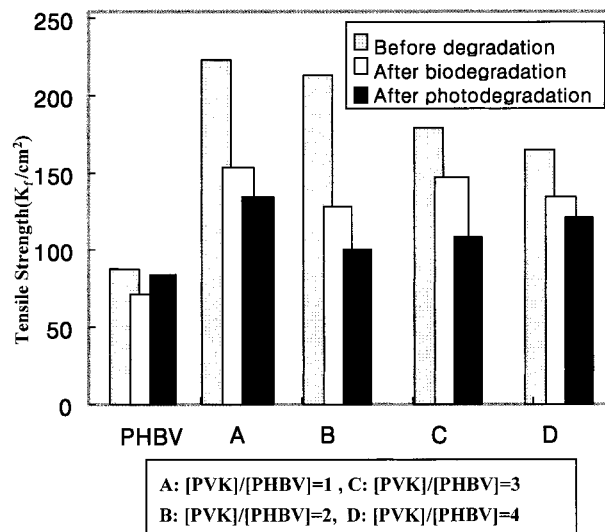


Figure 10 Tensile strengths of PHBV and P(HBV-*g*-PVK) before and after photo- or biodegradations.

CONCLUSIONS

Graft copolymers, P(HBV-*g*-PVK)s, were synthesized by graft copolymerization of PVK onto PHBV under nitrogen atmosphere using BPO as an initiator. The highest grafting efficiency was obtained at 3:1 weight ratio of PVK to PHBV in feed. The initial decomposition temperature of P(HBV-*g*-PVK) was 272°C. In the photodegradation test of P(HBV-*g*-PVK), the color differences of P(HBV-*g*-PVK) showed higher value than that of PHBV. After exposure under UV light irradiation for 100 h, the film surfaces of P(HBV-*g*-PVK) exhibited the many pits due to the photodegradation property of PVK moiety in P(HBV-*g*-PVK). In the biodegradation test of P(HBV-*g*-PVK), the film surface of the P(HBV-*g*-PVK) showed extensive grooves and pits as compared with the untreated P(HBV-*g*-PVK). The tensile strengths of P(HBV-*g*-PVK) after photo- and biodegradations was shown to be much lower compared with untreated samples. As a result, P(HBV-*g*-PVK) was found to have good photo- and biodegradability, maintaining the higher strength than PHBV.

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REFERENCES

- Huang, S. J. In *Comprehensive Polymer Science*; Allen, G., Bewington, J. C., Eds.; Pergamon Press: London, 1989; p 567.

2. Albertsson, A. C.; Karlsson, S. In *Comprehensive Polymer Science*; First Press: London, 1993.
3. Huang, S. J. *J Macromol Sci-Pure Appl Chem* 1995, A32(4), 593.
4. Karlsson, S.; Albertsson, A. C. *J Macromol Sci-Pure Appl Chem* 1995, A32(4), 599.
5. Tokiwa, Y.; Suzuki, T. *J Ferment Technol* 1974, 52, 393.
6. Tokiwa, Y.; Suzuki, T. *J Appl Polym Sci* 26, 444 (1981).
7. David, C.; Demarteau, W.; Gueskens, G. *Eur Polym J* 1970, 6, 537.
8. Lukac, I.; Hrdlovic, P.; Manasek, Z.; Bellus, D. *J Polym Sci A-1* 1971, 9, 69.
9. Dan, E.; Guillet, J. E. *Macromolecules*, 7, 1974, 230.
10. Randy, B.; Rabek, J. F. *Photodegradation, Photooxidation, and Photostabilization of Polymers*; Wiley: New York, 1975; chap 4.
11. Faure, J.; Fouassier, J. P.; Lougnot, D. J. *J Photochem* 1976, 5, 13.
12. Kiwi, J.; Schnabel, W. *Macromolecules* 1976, 9, 468.
13. Small, R. D.; Scaiano, J. C. *Macromolecules* 1978, 11, 840.
14. Guillet, J. E. *Naturwissenschaften* 1972, 59, 503.
15. Bae, Y. O.; Ha, C. S.; Cho, W. *J Eur Polym J* 1991, 27, 121.
16. Kang, D. I.; Ha, C. S.; Cho, W. *J Eur Polym J* 1992, 29, 5621.
17. Ha, C. S.; Choi, S. K.; Lim, D. S.; Cho, W. *J Appl Polym Sci* 1992, 45, 2159.
18. Park, D. J.; Bae, Y. O.; Ha, C. S.; Kim, B. K.; Cho, W. *J Polym (Korea)* 1992, 16(2), 235.
19. Park, D. J.; Ha, C. S.; Cho, W. *J Macromol Sci Chem* 1993, A30, 949.
20. Park, J. Y.; Son, H. H.; Lee, S. W.; Park, D. J.; Ha, C. S.; Cho, W. *J Polym (Korea)* 1993, 17, 720.
21. Park, J. Y.; Park, D. J.; Ha, C. S.; Cho, W. *J Appl Polym Sci* 1994, 51, 1303.
22. Park, D. J.; Ha, C. S.; Cho, W. *J Macromol Sci Chem* 1995, A32, 1317.
23. Park, D. J.; Ha, C. S.; Cho, W. *J Appl Polym Sci* 1998, 67, 1345.
24. Encanas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules* 1979, 12, 1167.
25. Dipak, A.; Raval, K. *J Macromol Sci-Pure Appl Chem* 1988, 35, 2201.
26. Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980; p 12.
27. Park, D. J.; Lee, N. J.; Ha, C. S.; Cho, W. *J Appl Polym Sci* 1992, 44, 727.
28. Park, D. J.; Ha, C. S.; Cho, W. *J Appl Polym Sci* 1994, 54, 763.
29. Lee, S. W.; Park, D. J.; Ha, C. S.; Cho, W. *J Appl Polym Sci* 1995, 58, 1409.
30. Saltzman, B. *Principles of Color Technology*, 2nd ed.; Wiley—Interscience: New York, 1981.
31. ASTM standard D 1924-70 (April 1970), American Society for Testing and Materials, Philadelphia, PA 19103, 1970.
32. Schofield, F. *Natl Paint Varnish Lacquer Assoc Sci Soc Circular* 1943, 644.
33. Golemba, F. J.; Guillet, J. E. *Macromolecules* 1972, 5, 212.
34. Heskins, M.; Guillet, J. E. *Macromolecules* 1972, 3, 224.