Effect of ^{60}Co γ-Radiation on the Properties of Poly(hydroxybutyrate-*co*-hydroxyvalerate)

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ABSTRACT: The effects of ^{60}Co γ-radiation on the properties of poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), including the chemical, mechanical, and thermal properties, were investigated. Molecular weight of the irradiated PHBV as measured using a Ubbelohde-type capillary viscometer decreased significantly. Fourier transform infrared–attenuated total reflection (FTIR–ATR) and ^{1}H nuclear magnetic resonance (NMR) spectra show that chain scission was the predominant reaction in the PHBV irradiated with 10 and 25 MRad doses. The $G(S)$ value for the chain scission was 0.9, and the number of bond cleavages per molecule was 0.22 MRad^{-1}. Thermal and tensile properties of control and irradiated PHBV were examined using a differential scanning calorimeter (DSC) and an Instron tensile testing machine, respectively. Results indicate that ^{60}Co γ-radiation significantly affected the thermal and tensile properties of PHBV. The melting temperatures of the irradiated PHBV decreased. Tensile strength and fracture strain of the irradiated PHBV decreased dramatically, indicating increased brittleness. The fracture surfaces studied using a scanning electron microscope (SEM) showed some voids and a brittle fracture surface. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1059–1067, 1999

Key words: poly(hydroxybutyrate-*co*-hydroxyvalerate); γ-radiation; chain scission; thermal properties; tensile properties

INTRODUCTION

Poly(hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate (PHBV) are produced from a variety of microorganisms.[1,2] These polymers are degradable in normal environment, either by hydrolytic or enzymatic degradation processes.[3] They have mechanical properties comparable to traditional polymers, such as polypropylene and polyethylene, and can be formed into films, fibers, and sheets.[4,5]

^{60}Co γ-radiation has been used to change the mechanical and physical properties of amorphous polymers.[6–10] The molecular changes induced by γ-radiation in a polymer may be classified as (1) main chain bond scission, resulting in a decrease in molecular weight and, thus, adversely affecting its mechanical properties, and (2) chain crosslinking, resulting in an increase in molecular weight and formation of network structure. Both chain scission and crosslinking occur primarily in the amorphous region, while some may take place in the boundary between the crystalline and amorphous regions.[6]

It must be stressed that the two mechanisms, chain scission and crosslinking, depend on the radiation dose, the radiation temperature, and the type of the polymer. Chain scission has been shown to occur in a polymer at low radiation dose, while crosslinking occurs at high radiation dose.[7] At temperatures below T_g, crosslinking is retarded because of the lower chain mobility; while

at temperatures above T_g, the crosslinking rate increases significantly with the increased chain mobility.[8] Parkinson and Sisman[9] found that aromatic compounds, in general, were more resistant to radiation compared to aliphatic compounds primarily because of the phenyl ring. Netravali and Manji,[10] who studied the effect of γ-radiation on graphite fibers, epoxy resin, and their interfacial strength, found no effect of γ-radiation on the strength of the fibers, but they found an adverse effect on the mechanical properties of epoxies. Their study also indicated increased graphite fiber–epoxy interfacial strength as a function of the radiation dosage and the creation of polar groups in the resin.

Carswell et al.[11–14] and Koning et al.[15] conducted extensive studies on the radiation chemistry of poly(hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate. They observed the formation of volatile products, such as carbon monoxide, carbon dioxide, and hydrogen, upon the radiolysis of these polymers.[12,14] The reduction in the average molecular weight suggested that the chain scission was the predominant reaction in the polymers.[12,14] Using the electron spin resonance (ESR) technique, they observed the formation of radicals on the main chain of the polymers as a result of the radiolysis at 77 K.[11–13] Their nuclear magnetic resonance (NMR) results indicated the evidence of the formation of new saturated end groups, resulting from the scission of the main chain ester groups.[14]

This article examines the effects of ^{60}Co γ-radiation on the chemical, tensile, and thermal properties of PHBV. Properties of control and irradiated PHBV were characterized using a Ubbelohde-type capillary viscometer, Fourier transform infrared (FTIR) spectrometer with a SplitPea™ accessory for attenuated total reflection (ATR), ^{1}H-NMR, Instron tensile testing machine and differential scanning calorimeter (DSC).

EXPERIMENTAL

PHBV was provided by the BIOPOL business unit of Monsanto. 1-mm-thick PHBV films were formed using a hot press at 180°C under 140 MPa for 5 min. The films, after forming, were stored at room temperature for over 1 month to allow the completion of crystallization.[16] Following that period, the PHBV films were exposed to ^{60}Co γ-radiation with 10 and 25 MRad doses in air and at room temperature in the Ward Laboratory for Nuclear Studies at Cornell University.

Control and irradiated PHBV specimens were dissolved in chloroform, and the viscosity of the solution was measured using a Ubbelohde-type capillary viscometer designed to need no kinetic energy correction. All the data were obtained in chloroform at 30°C. Weight-average molecular weight ($\overline{M_w}$) was calculated according to the following equation[17]:

$$[\eta] = 1.18 \times 10^{-4}\, \overline{M_w^{0.78}} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity.

High-resolution ^{1}H-NMR spectra were obtained using a Bruker/Tecmag 300 spectrometer operating at 300 MHz. Deuterated chloroform was used as the solvent and tetramethylsilane (TMS) as the internal reference. FTIR–ATR spectra were obtained using a Nicolet Magna 560 FTIR spectrometer with a SplitPea™ accessory for ATR. FTIR–ATR spectra were averages of 32 scans recorded at a resolution of 2 cm^{-1} in the range of 4000 to 500 cm^{-1}.

Strips with dimensions of $90 \times 10 \times 1$ mm were cut from control and irradiated PHBV films for tensile testing. Wood tabs were glued to both ends of the strips to avoid jaw breaks. The gauge length was 50 mm. Tensile tests were performed using an Instron tensile testing machine (Model 1122) according to ASTM D 3039-76 at a strain rate of 0.04 min^{-1}. Average values were calculated from at least five specimens. The fracture surface topographies of the tensile specimens were investigated using a Leica 440 scanning electron microscope (SEM).

Thermal analysis was performed using a Perkin–Elmer differential scanning calorimeter, DSC-4, calibrated with Indium. Specimens were heated from 50 to 180°C at a heating rate of 10°C/min for the first run. After being held at 180°C for 2 min, the specimens were cooled down to 50°C at a cooling rate of 10°C/min. Then specimens were reheated to 180°C at the same heating rate of 10°C/min for the 2nd run. Melting temperature, T_m, values were obtained from the onsets of the first and second peaks of both first and second runs. Melting enthalpy, ΔH_m, values were obtained from both first and second runs.

Table I   Effect of ^{60}Co γ-Radiation on the Chemical Properties of Poly(hydroxybutyrate-*co*-hydroxyvalerate)

Dose (MRad)	$[\eta]$ (dL/g)	$\overline{M_w} \times 10^{-4}$ (g/mol)	Average Bond Cleavages per Molecule per MRad (N)	$G(S)$ Value
0	1.885	24.49		
10	0.763	7.68	0.22	0.9
25	0.432	3.70		

RESULTS AND DISCUSSIONS

Chemical Analysis

Table I shows the intrinsic viscosity $[\eta]$ of PHBV measured using a Ubbelohde-type capillary viscometer and the weight-average molecular weight $\overline{M_w}$ calculated using eq. (1). It can be seen from Table I that $\overline{M_w}$ decreased from 24.49×10^4 g/mol for control specimen to 7.68×10^4 g/mol for specimen irradiated with 10 MRad dose and to 3.70×10^4 g/mol for specimen irradiated with 25 MRad dose.

As discussed earlier, ^{60}Co γ-radiation may induce chain scission and/or crosslinking in a polymer. Chain scission, in general, occurs to polymeric chains at a low radiation dose. At high doses, free radicals could be generated on polymeric chains, which may cause crosslinking by forming covalent bonds between polymer chains.[7] The data in Table I show that both $[\eta]$ and $\overline{M_w}$ decrease dramatically, indicating that the chain scission was the predominant reaction in the PHBV irradiated with 10 and 25 MRad. These results are in good agreement with those reported by Carswell et al.[14]

$G(S)$ and $G(X)$ represent the number of chain scission and crosslinking per 100 eV of energy absorbed in a polymer, respectively, and can be calculated from the changes in the average molecular weight $\overline{M_n}$ and $\overline{M_w}$ with the radiation dose used.[14,18] If the chain scission is random and the polydispersity index of the polymer is equal to 2, plots of $1/\overline{M_n}$ and $1/\overline{M_w}$ versus the radiation dose used is linear. In the absence of crosslinking in the present case, the value of $G(X)$ was assumed to be 0. The $G(S)$ value of 0.9 was calculated from the $\overline{M_w}$ data using equations given by Carswell et al.[14] and Saito.[18] This $G(S)$ value was lower than those $G(S)$ values of 2.7 for the PHBV containing 19% hydroxyvalerate and 1.3 for the PHB, as reported by Carswell et al.[14] The $G(S)$ value depends on the crystallinity of the polymers since only the amorphous part is affected by the radiation. The PHBV used in this study containing 9% hydroxyvalerate is presumed to have a higher crystallinity, resulting in a lower $G(S)$ value.

The average number of bond cleavages per original PHBV molecule per MRad dose N can be given by the following eq. (2).[19]

$$N = \frac{\overline{M_w(0)}}{\overline{M_w(D)}} - 1 \qquad (2)$$

where $\overline{M_w(0)}$ and $\overline{M_w(D)}$ are the values of the weight-average molecular weight of PHBV at 0 and D radiation doses, respectively. The average N value was 0.22 MRad^{-1} for both 10 and 25 MRad doses, as presented in Table I.

Typical FTIR–ATR spectra of control and irradiated PHBV are presented in Figure 1. Except for the bands around 600 cm^{-1}, no changes are seen between the control and the irradiated PHBV spectra. The change of the bands around 600 cm^{-1} could result from the difference in the crystallinity between the control and the irradiated PHBV. The bands between 2800 and 3000 cm^{-1} regions, which are the stretching of C—H bond on PHBV main chain, show no change. There may be no major chemical structure change in the irradiated PHBV as seen from the FTIR–ATR spectra. Using the ESR technique, Carswell et al.,[11–13] Koning et al.,[15] and Malcolm and Wormald[20] have observed radical formation in polymers on radiolysis. In the present case, there may be lack of radicals due to the low radiation dose used; and, as a result, we have assumed no crosslinking by the combining of radicals. This is confirmed by the $\overline{M_w}$ observations, which showed molecular cleavage continuing at the same rate up to 25 MRad dose.

Figure 1   Typical FTIR–ATR spectra of poly(hydroxybutyrate-*co*-hydroxyvalerate): (a) control, (b) irradiated with the 10-MRad dose, and (c) irradiated with the 25-MRad dose.

Both control and irradiated PHBV also show no changes in their ^{1}H-NMR spectra. Figure 2 shows the ^{1}H-NMR spectra of the irradiated PHBV. From the ^{1}H-NMR spectra, no new structures were observed, which was opposite to the results reported by Carswell et al.[14] The maximum dose used in the present study was 25 MRad, which was much lower compared to the doses used by Carswell et al.[14] From the ^{1}H-NMR results, it can be concluded that the concentration of the new structures formed would be absent or too low to be observed. Hydroxyvalerate content was calculated from the integration of H peaks of CH_3 of hydroxybutyrate and hydroxyvalerate, as indicated in Figure 2, and was 9.1% for both control and irradiated PHBV. Therefore, the chain scission appears to be completely random; that is, chain scission may occur equally in the hydroxybutyrate and hydroxyvalerate units of PHBV exposed to γ-radiation.

The chain scission mechanism may be as proposed in Figure 3. At high doses, with further chain scission of the carboxyl acid, volatile products, such as carbon dioxide, carbon monoxide, and hydrogen, would be formed. Volatile products, such as ethane, propane, and butane, were

also observed by Carswell et al.,[14] which probably resulted from the scission of side chains in the polymers. Compared to the radical formation site on aliphatic group (CH_2) of PHBV main chain,[13,20] the bond cleavage in the ester groups may be easier. Further, there may be some crosslinking at high doses by radical combination, as observed by Carswell et al.[14]

Thermal Properties

Typical DSC thermograms of the first and second heating runs are presented in Figure 4. Table II summarizes the thermal properties of control and irradiated PHBV. It can be seen from Figure 4 that in the first run, both control and irradiated PHBV show two melting peaks indicative of two crystal sizes. However, in the second run, control PHBV demonstrates only one peak, while the irradiated specimens show two peaks. Melting temperatures of both the first and the second peaks, in both first and second runs, of irradiated PHBV are much lower than that of control PHBV.

Melting temperature of a semicrystalline polymer is primarily a function of the crystal size. In the present study, both control and irradiated

Figure 2 ¹H-NMR spectra of poly(hydroxybutyrate-co-hydroxyvalerate) irradiated with the 25-MRad dose.

(a) bond cleavage on hydroxybutyrate unit

(b) bond cleavage on hydroxyvalerate unit

Figure 3 Scheme of chain scission of poly(hydroxybutyrate-*co*-hydroxyvalerate) induced by [60]Co γ-radiation.

PHBV specimens had the same thermal history and, hence, were expected to have the same crystal size, provided there was no effect of radiation on crystals. The two melting peaks as shown in the DSC thermograms resulted from two crystal sizes formed during the quick cooling in the film preparation. As discussed earlier, [60]Co γ-radiation induced chain scission occurred in the amorphous region. This resulted in less entangled chains in the amorphous regions, lower glass transition temperature, and less constraints on the crystals of PHBV. Further, it created a broader molecular weight distribution with higher M_w species from the crystalline region and lower M_w species from the amorphous region due to the chain scission. Also, γ-radiation is probably responsible for introducing defects in the crystalline region. As a result, the first and second melting temperatures of PHBV irradiated with 10 MRad dose are 5.7 and 6.1°C lower than those of control specimen, respectively. The first and second melting temperatures of PHBV irradiated with 25 MRad dose are 11.7 and 9.8°C lower than those of control specimen, respectively. Table II shows that in the first run, ΔH_m is 50.32, 48.52, and 46.09 J/g for specimens irradiated with 25, 10, and 0 MRad (control) doses, respectively. This indicates that although the crystal size is small, the crystallinity increased after radiation. As suggested by the viscosity results, γ-irradiated PHBV specimens had a lower molecular weight and, therefore, are much easier to crystallize than the control specimen. At room temperature, above the T_g of PHBV, instead of existing crystal growing, the radiation seemed to produce new nucleating

Figure 4 Typical DSC thermograms of poly(hydroxybutyrate-*co*-hydroxyvalerate): (a) first and (b) second runs; (1) control; (2) irradiated with the 10-MRad dose; (3) irradiated with the 25-MRad dose.

Table II   Effect of ^{60}Co γ-Radiation on the Thermal Properties of Poly(hydroxybutyrate-*co*-hydroxyvalerate)

Dose MRad	First Run			Second Run		
	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
0	146.5	155.9	46.09	149.1	—[a]	46.38
10	140.8	149.8	48.52	143.0	154.1	44.50
25	134.8	146.1	50.32	136.3	147.9	44.87

T_{m1}, T_{m2}, and ΔH_m are the onsets of first and second peaks and the melting enthalpy, respectively.
[a] Not detected.

sites, which resulted in smaller crystal size but higher crystallinity in the irradiated specimens compared to control specimens.

From Table II, it can be seen that in the second run, the melting temperature was 149.1°C for control PHBV, whereas the second melting peak was not seen. However, melting temperatures of 143 and 154.1°C were observed for specimens irradiated with the 10-MRad dose, and 136.3 and 147.9°C were observed for specimens irradiated with the 25-MRad dose. As discussed above, chain scission mostly occurred in the amorphous region. As a result, irradiated PHBV likely had a broader molecular weight distribution and was possibly responsible for forming two crystal sizes. Control PHBV had a narrower molecular weight distribution and probably formed only one crystal size. Control PHBV, in the second run, had a slightly higher melting enthalpy than the specimens irradiated with the 10- and 25-MRad doses.

Tensile Properties

Typical stress versus strain plots of control and irradiated PHBV are presented in Figure 5. Table III summarizes the tensile properties of control and irradiated PHBV. Tensile strength decreased from 31.69 MPa for control to 24.24 MPa for spec-

Figure 5   Typical tensile stress versus strain plots of poly(hydroxybutyrate-*co*-hydroxyvalerate): (a) control; (b) irradiated with the 10-MRad dose; (c) irradiated with the 25-MRad dose.

Table III   Effect of ^{60}Co γ-Radiation on the Tensile Properties of Poly(hydroxybutyrate-*co*-hydroxyvalerate)

Dose (MRad)	σ_{max} (MPa)	E (GPa)	ε_{break} (%)	Gc (MPa)
0	31.69	1.90	3.52	0.77
	(0.43)[a]	(0.05)	(0.43)	(0.12)
10	24.24	1.91	1.75	0.25
	(1.24)	(0.08)	(0.20)	(0.05)
25	12.57	1.87	0.73	0.05
	(1.07)	(0.05)	(0.08)	(0.01)

[a] Numbers in the parenthesis are the standard deviations.

imens exposed to the 10-MRad dose, and to 12.57 MPa for specimens exposed to the 25-MRad dose. Fracture strain decreased from 3.52% for control to 1.75 and 0.73% for specimens exposed to the 10- and 25-MRad doses, respectively. Fracture toughness decreased from 0.77 MPa for control to 0.25 and 0.05 MPa for specimens exposed to 10 and 25-MRad doses, respectively. Young's modulus showed a small increase for PHBV irradiated with 10 MRad dose, and a small decrease for PHBV irradiated with 25 MRad dose.

As discussed above, significant chain scission took place in the amorphous region of irradiated PHBV, which resulted in a dramatic decrease of molecular weight, causing much less chain entanglement chains in the amorphous region. The crystal size also decreased with the radiation dose. As a result, tensile strength, fracture strain, and fracture toughness of irradiated PHBV specimens were much lower than those of control PHBV specimens. Compared to control PHBV, irradiated PHBV showed very little change in Young's modulus because Young's modulus of a polymer depends more on its crystallinity than the amorphous region.

Figure 6(a) to (c) show the SEM photomicrographs of the fracture surface of irradiated and control PHBV specimens. Fracture surface of control PHBV specimens shown in Figure 6(a) is rougher than that of the specimens irradiated with 10 MRad dose [Fig. 6(b)]. Specimens irradiated with the 25-MRad dose demonstrated the most brittle fracture [Fig. 6(c)]. Voids may be clearly seen in Figure 6(c) of the fracture surface of the specimens irradiated with the 25-MRad dose. These voids may be the result of the gas products formed by chain scission during the radiation as observed by Carswell et al.[14] Chain

(a) control

(b) irradiated with 10 MRad dose

(c) irradiated with 25 MRad dose

Figure 6   SEM photomicrographs of the fracture surfaces of poly(hydroxybutyrate-*co*-hydroxyvalerate).

scission and local stress built up by the voids were responsible for the brittle fracture of irradiated PHBV.

CONCLUSIONS

The effects of ^{60}Co γ-radiation in air, at room temperature, on the properties of PHBV have been characterized. The main conclusions of the study may be summarized as below.

1. ^{60}Co γ-radiation causes random chain scission in PHBV. The $G(S)$ value was 0.9, and the number of bond cleavages per molecule was 0.22 MRad^{-1}. No crosslinking reactions were seen up to the 25-MRad dose.
2. Melting temperatures of irradiated PHBV in both first and second runs were much lower than those of control PHBV, indicating smaller crystal size after radiation.
3. Tensile strength, fracture strain, and fracture toughness of irradiated PHBV were much lower than those of control PHBV because of the chain scission. Young's modulus, however, showed no significant change.
4. SEM photomicrographs demonstrate a much brittle fracture of irradiated PHBV as a result of lower molecular weight and voids generated during radiation treatment.

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