# Effect of Gamma Irradiation on the Mechanical Properties and Thermal Properties of Poly(3-Hydroxybutyrate-Co-3-hydroxyhexanoat e)(PHBHHx) Based Films

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**Abstract.**Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) is a naturally sourced polymer with good biocompatibility and potential applications in biomedical field after sterilization. Radiation sterilization technology has been extensively applied on medical products. However, for polymer-based biomedical materials, gamma irradiation can cause random chain scission on the polymer backbone. In this paper, we studied the effect of gamma irradiation on the mechanical and thermal properties of PHBHHx. The tensile strength and fracture strain of PHBHHx decreased after irradiation, while the brittleness increased after irradiation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results showed that the melting temperatures of irradiated PHBHHx are lower than the non-irradiated films, but the irradiated specimen shows a higher decomposition temperature than non-irradiated PHBHHx.

## 1 Introduction

Polyhydoxyalkanoates (PHAs) are polyesters produced by microorganisms under unbalanced growth conditions. The polymers are generally biodegradable and have good biocompatibility, which makes them attractive for biomedical applications. Several PHAs have been applied in biomedical field as implant materials, including poly 3-hydroxybutyrate (PHB), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), poly

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4-hydroxybutyrate (P4HB), poly(3-hydroxyoctanoate) (PHO), and PHBHHx. PHBHHx was reported to have better performance over all other PHAs as mentioned above.

Biological materials must be sterilized before use. The traditional sterilization method, such as gas sterilization with ethylene oxide and steam sterilization, are not suitable for PHBHHx-based films. Gamma irradiation is the standard method in the medical device industry as it is cost-effective, and can be applied at room temperature.

However, gamma irradiation can cause random chain scission or chain crosslinking on the polymer backbone. The aim of this study is to investigate the effect of gamma irradiation on the properties of PHBHHx by thermal and mechanical analysis.

## 2 Experimental

### 2.1 Materials

PHBHHx containing 12% hydroxyhexanoate was kindly donated by department of biological science and biotechnology of Tsinghua University (produced by Shantou Lianyi Biotech Co., Guangdong, China). PHBHHx was purified before use: PHBHHx was dissolved in chloroform under vigorous agitation for 2 h at 65 $^{o}$C, then precipitated in methanol, and finally dried under vaccum. Purified PHBHHx is a white powder. All other solvents were of analytical grade.

### 2.2 Film preparation and irradiation

Sample films were prepared by solution casting method. All samples were irradiated in sealed packaging using a $^{60}$Co source at the Department of Applied Chemistry of Peking University at room temperature, and the dose was 25, 45, and 70 kGy.

### 2.3 Methods

The spectra were obtained with an accumulation of 100 scans and with a resolution of 4 $cm^{-1}$. The tensile properties of PHBHHx films were measured by a SANS universal testing machine with a loadcell of 100N with a strain rate of 20 mm/min. The differential scanning calorimetry (DSC) studies were carried out at heating ramp 10 $^{o}$C $min^{-1}$ from 0 $^{o}$C to 150 $^{o}$C using a Mettler-Toledo DSC 1. Thermogravimetric analysis (TGA) on PHBHHx films were performed with Shimadzu TGA-50 thermal analyzer under a nitrogen atmosphere with a heating speed of 10 $^{o}$C·$min^{-1}$.

# 3 Results and discussion

## 3.1 Infrared spectroscopy

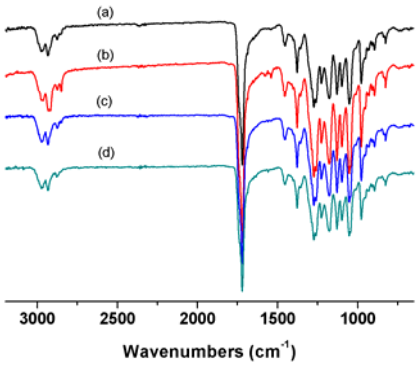


Fig. 1 ATR-FTIR spectra of control PHBHHx and irradiated PHBHHx: (a) control PHBHHx, (b) irradiated with 25 kGy dose, (c) irradiated with 45 kGy dose, (d) irradiated with 70 kGy dose.

Fig. 1 shows the ATR-FTIR spectras of control PHBHHx and irradiated PHBHHx films.. All infrared absorption peak of irradiated specimens can be found in control specimen spectra, suggesting that there is no significant change between the control and the irradiated specimens. The absorption peaks of 2976 $cm^{-1}$, 2933 $cm^{-1}$, 2875 $cm^{-1}$, is the stretching of C-H bond. The results indicate that there is no major change of chemical structure between non-irradiated PHBHHx and PHBHHx samples irradiated with either 25 kGy, 45 kGy, or 70 kGy dose.

## 3.2 Mechanical behavior

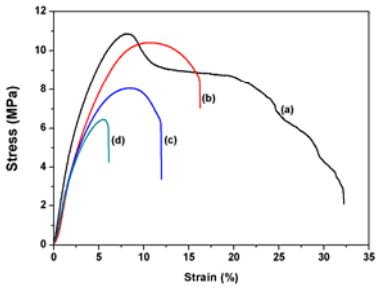


Fig. 2 The tensile stress versus strain plots of control and irradiated PHBHHx: (a) control, (b) irradiated with 25 kGy dose, (c) irradiated with 45 kGy dose, (d) irradiated with 70 kGy dose.

.Tensile testing is very useful to determine how gamma irradiation affects the mechanical properties of PHBHHx films. Fig. 2 shows the typical stress-strain plots of control and irradiated PHBHHx films. Mechanical properties are generally characterized by two parameters, the tensile strength and the elongation at break. Table 1 summarizes the two parameters of the control and irradiated specimens. As shown in Fig. 2 and Table 1, the elongation at break reduced from 49.13% for non-irradiated PHBHHx to 19.11%, 11.89%, and 6.14% for PHBHHx irradiated with 25 kGy, 45 kGy, and 70 kGy, respectively. The elongation at break of the irradiated PHBHHx with 70kGy is even lower than 10%, which can be classified as brittle. The tensile strength decreased from 8.76 for non-irradiated PHBHHx to 7.10 for irradiated one with the increase of irradiation dose, except for the PHBHHx irradiated with 25 kGy. We assume that significant chain scission took place in the amorphous regions of the irradiated PHBHHx samples, which resulted in a dramatic decrease in molecular weight, leading to less chain entanglements in amorphous regions. As a result, the tensile strength of the irradiated PHBHHx samples were slightly lower than those non-irradiated PHBHHx sample.

Table 1 Mechanical Properties Of Control Phbhhx And Irradiated Phbhhx

| Dose (kGy) | tensile strength (MPa) | elongation at break (%) |
|---|---|---|
| 0 | 8.76 | 49.13 |
| 25 | 10.18 | 19.11 |
| 45 | 8.11 | 11.89 |
| 70 | 7.10 | 6.14 |

## 3.3 Thermal behavior

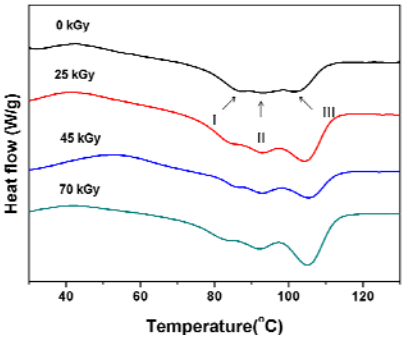


Fig. 3 Melting curves for control PHBHHx and irradiated PHBHHx. Peaks I, II, and III denote the low-, middle- and high-temperature melting, respectively.

Three melting peaks were observed in the DSC heating cruves for control and irradiated specimens as reported (Fig. 3), the occurrence of peak I was a result of the melting of crystals formed upon long-time annealing, the other two main melting edothermic peaks II and III are caused by the model of melting, recrystallization and remelting of PHB crystals during the heating process. With the increase of irradiated dose, the melting temperature of peak I shifted towards a lower temperature. A similar shift was also observed in peak II, which may due to the decrease of PHBHHx crystal size.

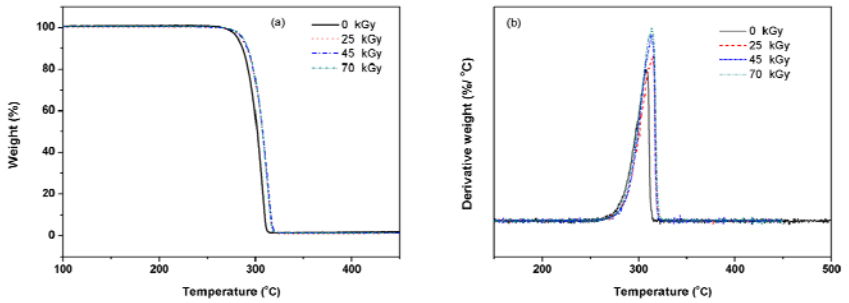


Fig. 4 TGA (a) and DTG (b) curves of. control and irradiated PHBHHx to the indicated doses.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves are shown in Fig. 4. The TGA curves of irradiated specimens shifted towards a higher temperature compared to control specimen (Fig. 4a), the initial decomposition temperature of PHBHHx irradiated with 70 kGy located at 287.16 $^{o}$C, which is 6 $^{o}$C higher than that of control specimen (281.28 $^{o}$C ). The derivation of the thermal decomposition curve (Fig. 4b) shows the difference of peak temperatures between the irradiated and non-irradiated samples. The temperature of total weight loss of the control PHBHHx sample was 308.45 $^{o}$C, and the value of irradiated PHBHHx with 25 kGy, 45 kGy, and 70 kGy are 314.70 $^{o}$C, 314.05 $^{o}$C, and 313.93 $^{o}$C, respectively. We also notice that the irradiated specimen shows a slightly higher decomposition temperature than the control PHBHHx, indicating that the scissions that occur due to gamma irradiation do not affect the thermal decomposition temperature of the sample.

## 4 Conclusion

We have studied the effect of gamma irradiation on the structure and properties of PHBHHx films. The mechanical studies showed that tensile strength and fracture strain of PHBHHx decreased after irradiation with the increase of brittleness.

Thermogravimetric analysis and differential scanning calorimetry results showed that the melting temperature ($T_m$) of PHBHHx films decreased with the increase of irradiation dose,

due to the decrease of PHBHHx crystal size.

## 5 Acknowledgements

The authors greatly acknowledge the support of the Beijing Key Laboratory of Radiation Advanced Materials of Beijing Research Center for Radiation Application.

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