The gamma irradiation effects on structural and optical properties of silk fibroin/HPMC blend films

G. Rajesha Shetty, B. Lakshmeesha Rao, Mahadeva Gowda, C. S. Shivananda, S. Asha, K. Byrappa, and Y. Sangappa

Citation: AIP Conference Proceedings **1731**, 070015 (2016); doi: 10.1063/1.4947847
View online: http://dx.doi.org/10.1063/1.4947847
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1731?ver=pdfcov
Published by the AIP Publishing

The Gamma Irradiation Effects on Structural and Optical Properties of Silk Fibroin/HPMC Blend Films

G Rajesha Shetty[1], B Lakshmeesha Rao[2], Mahadeva Gowda[2], C S Shivananda[2], S Asha[2], K. Byrappa[2], Y. Sangappa [2,3*]

[1]*Department of Physics, Govt. First Grade College, Hiriadka, Udupi - 576 113, India*
[2]*Department of Studies in Physics, Mangalore University, Mangalagangotri, Mangalore - 574* 199*, India*
[3]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*
**Corresponding Author: syhalabhavi@yahoo.co.in*

Abstract. In this paper the structural, chemical and optical properties of gamma irradiated silk fibroin/Hydroxypropyl methyl cellulose (SF-HPMC) blend films were studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy. The results indicate that the gamma radiation did not affect significantly the primary structure of polypeptide arrangement in the blend films. But the optical properties of the blends changed with gamma irradiation dosage.

Keywords: Silk fibroin films, Structural properties, Thermal properties
PACS: 82.35.Pq; 61.80.-x; 61.05.cp; 81.70.Pg

INTRODUCTION

Silk consists of two kinds of proteins: silk fibroin a core material and sericin a glue like binding material. Recently silk fibroin is used in many forms, fibers, powders, films etc. [1]. Silk based films exhibit good thermal and chemical resistance, but they do not show properties of rigidity and mechanical strength by themselves that is essentially required for structural applications. Although silk fibers have excellent strength and flexibility, the water based regenerated silk materials are generally brittle in the dry state, having poor mechanical properties. If the dry state is required and the brittleness is undesirable, SF properties can be improved by blending SF solution with other polymers [2]. The improvement in properties of the blend depends on the degree of compatibility or miscibility of the polymers at the molecular level. Depending upon the degree of molecular mixing, blends can be compatible, semi-compatible or incompatible [3]. The gamma irradiation can be performed in order to investigate the effect of gamma radiation on the silk fibroin blends, which may be useful for development of the irradiated silk fibroin blends for biomedical applications in the future.

Most of the commonly used sterilization methods for silk include steam, ethylene oxide and gamma ray radiation [4]. Some studies have shown that gamma radiation can modify the chemical, physical and mechanical properties of silk fibroin [5]. Therefore, gamma irradiation method can be used as potential tool for improving the properties of silk and silk blends.

The goal of this study was to prepare and characterize SF/HPMC blend films, aiming at an insoluble film, with a more stable and crystalline structure. Later the blend film was exposed to gamma radiation of different doses. The films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy to evaluate their structural and optical properties.

EXPERIMENTAL

The *Bombyx mori* CSR4 bivoltine cocoons were cut into small pieces and then treated with boiling aqueous solution of 0.02M Na_2CO_3 to extract the glue like sericin protein and dried in hot air oven. The degummed silk is dissolved in 9.3M LiBr solution. This silk fibroin solution was dialyzed in water using a dialysis cassette in order to remove salt. Finally obtained optically clear solution was centrifuged to remove the small amount of silk aggregates formed during the process.

DAE Solid State Physics Symposium 2015
AIP Conf. Proc. 1731, 070015-1–070015-3; doi: 10.1063/1.4947847
Published by AIP Publishing. 978-0-7354-1378-8/$30.00

The equal quantity of solutions of SF [5 wt%] and HPMC [5 wt%] were mixed for 30 minutes with constant stirring at room temperature. The blend films were prepared by casting the mixed solutions onto polystyrene plates and allowing the solvent to evaporate at room temperature. Finally, the dried samples were gamma irradiated with 100 and 200 kGy.

RESULTS AND DISCUSSIONS

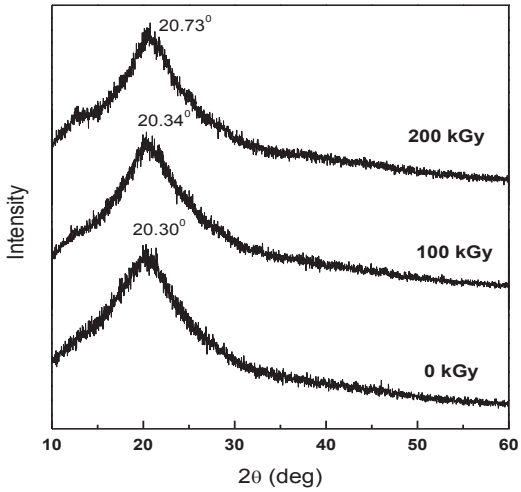

FIGURE 1. XRD spectra of virgin and gamma irradiated SF-HPMC blend films.

The XRD pattern of virgin and gamma irradiated SF-HPMC blend films at different doses are shown in Fig.1. The main prominent diffraction peak occurs at around 2θ = 20 in virgin and gamma irradiated blends [6]. From the XRD scans it is very clear that there is much change in the crystalline nature of the blends.

The full width at half maximum (FWHM) is generally associated with the crystallite size which can be obtained from Scherrer's formula [7]

$$L = \frac{k\lambda}{\beta \cos\theta} \qquad \text{a)}$$

where k=1, λ= 1.54A^0 and β=FWHM in radian.

.

TABLE 1. Structural parameters of virgin and gamma irradiated SF-HPMC blend films.

Sample	2θ (deg)	β (deg)	Crystallite size (Å)	Lattice strain (%)
0 kGy	20.30	11.28	7.5	0.2749
100kGy	20.34	10.27	8.2	0.2498
200kGy	20.73	10.05	8.4	0.2398

From the Table 1, it is evidenced that the crystallite size increases with increase in radiation dose. This may be due to the crosslinking reaction occurred in HPMC matrix due to gamma irradiation.

To investigate the conformational changes in SF and SF-HPMC blend for different doses of gamma radiation were characterized using FTIR spectroscopy. The FTIR spectra of virgin and gamma irradiated samples are shown in the Figure 2.

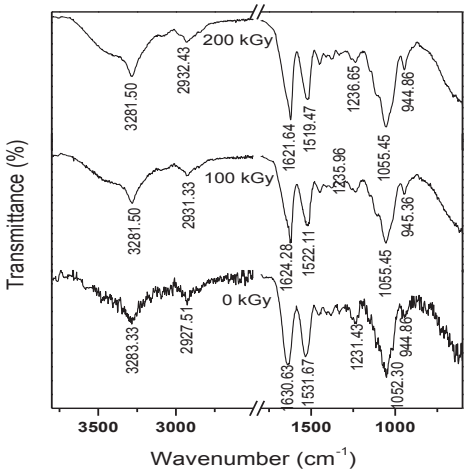

FIGURE 2. FTIR spectra of virgin and gamma irradiated SF- HPMC blend films

The SF-HPMC showed strong absorption bands at 1630 cm^{-1} (amide I), 1531 (amide II) and 1052 cm^{-1}, attributed to the silk II (β-sheet conformation) and 1231 cm^{-1} (amide III), attributed to (α-helical conformation) [6,8-9]. On the other hand, when the sample was irradiated for 100 kGy the absorption bands of amide I and amide II were shifted towards 1624 cm^{-1} and 1522 cm^{-1} respectively (more tendency of β sheet conformation), whereas the amide III band shift towards 1235 cm^{-1} (tendency towards silk I structure). The same result was found for gamma irradiation dose of 200 kGy with the absorption bands at 1621 cm^{-1}, 1519 cm^{-1}, 1236 cm^{-1} and 1055 cm^{-1}. This indicates that silk I and silk II structures are presented simultaneously in the virgin and gamma irradiated films; however, the poor solubility of SF-HPMC and crystallinity of the films indicates the predominance of silk II structure.

The UV absorption spectra of virgin and gamma irradiated SF-HPMC blend films are shown in Figure 3. The UV absorption peaks were located near 300 nm for all the blend films, and red shift was observed for the irradiated samples [10].

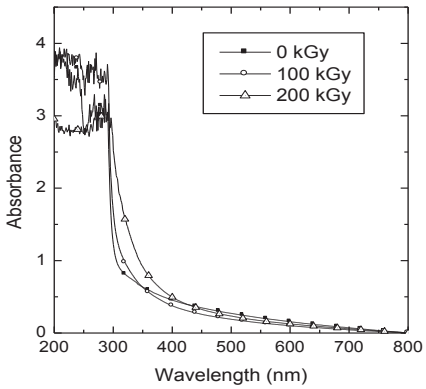

FIGURE 3. UV absorption spectra of virgin and gamma irradiated SF-HPMC blend films

UV-Vis plot of virgin and gamma irradiated samples were shown in Figure 3. The variation of optical energy gap was calculated for these samples according to method mention in earlier work [11]. The usual method of determination of value of E_g involves plotting $(\alpha h\nu)^{1/2}$ against hν. The plots of $(\alpha h\nu)^{1/2}$ versus hν near the absorption edge for films with different doses produce a linear fit. Extrapolating the straight regions of these relations to the hγ axis give the forbidden band gap E_g.

From the Figure 4, it is observed that the value of E_g decreased with the irradiation dose. This may be due to the crosslinking of polymeric chains [10].

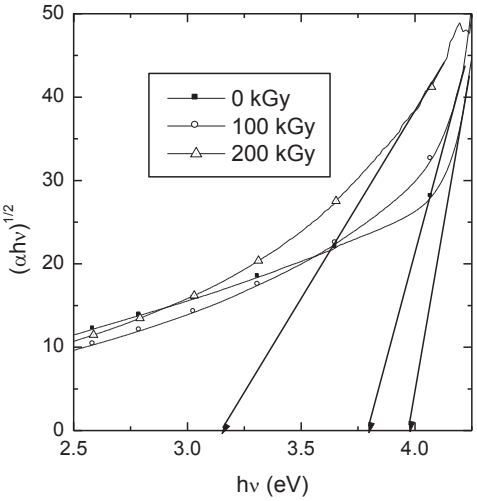

FIGURE. 4 The plots of $(\alpha h\nu)^{1/2}$ versus hν.

CONCLUSIONS

The SF-HPMC blend films were successfully prepared and gamma irradiation effects on structural, chemical and optical properties have been studied. A variation in the X-ray diffraction peak and intensity is observed for the irradiated blend films. The crystallite size found to be increased slightly after irradiation. The FTIR study indicates the predominance of silk II structure even after gamma irradiation. From the UV spectra we can conclude that forbidden band gap of SF-HPMC blend with equal concentration decreases with gamma dose.

REFERENCES

1. G. H. Altman, F. Diaz, C. Jakuba, T. Calabro, R. L. Horan, J. Chen, H. Lu, J. Richmond, and D. L. Kaplan, *Biomaterials*, **24**, 401 (2003).
2. K. Cai, K. Yao, Y. Cui, Z. Yang, X. Li, H. Xie, T. Qing, and L. Gao, *Biomaterials*, **23**, 1603 (2002).
3. M. S. Jayaprakash, K. Shivakumar and Shashidhar, *Indian Journal of Science and Technology* **6**, 3918-3922 (2013).
4. Y. M. Yang, Y. H. Zhao, X. H. Liu, F. Ding and X. S. Gu, *Journal of Applied Polymer Science* **104**, 1968-1972 (2007).
5. Y. Kawano, and A. J. M. Logarezzi, *Polymer Degradation and Stability* **50**, 125-130 (1995).
6. H. Y. Kweon, I. C. Um, and Y. H. Park, *Polymer* **42**, 6651-6656 (2001).
7. G. Torrado, S. Fraile, S. Torrado and S. Torrado, *Int. J. Pharm.***166**, 55-63 (1998).
8. X. X. Feng, L. L. Zhang, J. Y. Chen,Y. H. Guo, H. P. Zhang and C. I. Jia, *Biological macromolecules* **40**,105-111 (2007).
9. M. A. de-Moraes, G. M. Nogueira, R. F. Weska and M. M. Beppu, *Polymers* **2**, 719-727 (2010).
10. Sangappa, S. Asha, T. Demappa, G. Sanjeev, P. Parameswara and R. Somashekar, *Nucl. Inst. Meth. Phys. Res. B.* **267**, 2385-2389 (2009).
11. S. Asha, G. Sanjeev and Y. Sangappa, *Journal of Spectroscopy* **2015**, 7 (2015).