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Studies on the γ -Irradiated Polyvinyl Alcohol (PVA) Blended Gelatin Films

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Abstract

Different concentrations of PVA blended Gelatin were taken for grafting under γ-radiation. Better grafting means better cross-linking of polymer. We observed the effect of concentration of polymers and the effect of radiation doses. Various physico-mechanical and morphological properties like tensile strength (TS), elongation at break (Eb), FTIR, Scanning Electron Microscopy (SEM) of films were observed. For untreated (virgin) Film, radiation doses were optimized for such types of properties. By casting process Gelatin-based polyvinyl alcohol (PVA) films were prepared in different ratios. These films were irradiated under gamma radiation (^{60}Co) at different doses (0.5-5 kGy). The mechanical properties of these films were evaluated. It was found that 95% gelatin +5% PVA film exhibited the highest tensile strength (TS) value at 0.5 kGy gamma radiation (51 MPa), which was 46% higher than that of non-irradiated films.

Keywords: Radiation; Cross-linking; Polymer; Polyvinyl alcohol; Mechanical

Introduction

Polymer science and technology is one of the most active and promising fields in embracing a multitude of topics from natural polymers such as cellulose, wool, silk, jute etc. which are of utmost importance for living systems, to the synthetic high polymers [1,2]. Gelatin is one of the most versatile natural products known. Gelatin represents a typical renewable material from natural resources of animal origin. Gelatin was one of the first macromolecules employed in the production of biomaterials [3]. This biopolymer still attracts the attention of researchers because it is produced abundantly practically worldwide, has a relatively low cost and possesses excellent functional and filmogenic properties [3,4]. For this reason gelatin has been studied in film technology both alone [5-10] and in blends with other biopolymers [11]. Animal glue and gelatins normally contain about 15% of water and 1-4% of inorganic salts. They may also contain a small amount of grease. The main high molecular weight impurity that has been identified is a heat-coagulable mucoprotein complex.

Bone glues may contain as much as 6% of these materials. These impurities are of little or no importance in the majority of glue uses. The properties depend on the major protein constituent derived from the breakdown of collagen. This pure, and to some extent hypothetical, material is described here as gelatin (without an "e"). Gelatin then is regarded as the major protein constituent of gelatin and glue. The purest gelatins contains largely of gelatin and water. Gelatin, like its precursor collagen, contains carbon 15%, hydrogen 26%, nitrogen 18%, oxygen 25%, sulfur 0.1% and phosphorus traces (Figure 1).

Gelatin is a biopolymer, which possesses a number of properties. It has versatile application owing of its inherent properties. As a natural polymer it always gets priority for various applications. It degrades very quickly to the environment and this property makes some advantages and disadvantages for its application. Its water aging nature makes it alluring for bio medical implants. Therefore it is necessary to modify its quality and characteristic properties and improve its end products for diversified application like biomedical structural material. PVA is recognized as one of the few synthetic polymers truly biodegradable under both aerobic and anaerobic conditions. The irradiated blend films exhibit higher mechanical properties compared with the non-irradiated films [12]. Grafting of gelatin by various polymers has been studied with the objective of improving or modifying the properties of gelatin and in order to develop new materials combining the desirable properties of both natural and synthetic polymer. Many attempts, such as physical and chemical treatments, have lead to changes in the surface structure and surface energy of the films. Among them, physical treatments, such as ionizing or non-ionizing radiation, can introduce better surface cross-linking between natural and synthetic polymers, and reduce the hydrophilic nature of the film. Surface modification of the films can be carried out by the monomer treatment. The acrylate monomer 1,4-butanediol diacrylate (BDDA) induced cross-linking using their double bonds [13-16].

The present work was under taken to prepare a bio-synthetic blend of Gelatin with PVA, to modify its preparation and also modifying its quality and characteristic properties. For this reason, γ-radiation technique was applied. Gelatin and PVA are cheap, eco-friendly and available in Bangladesh. Considering all the factors, the ultimate goal of this research work is to improve the property of Gelatin through enhancement of tensile strength, elongation at break, stability etc. and finding its possibilities as bio medical material for implementation.

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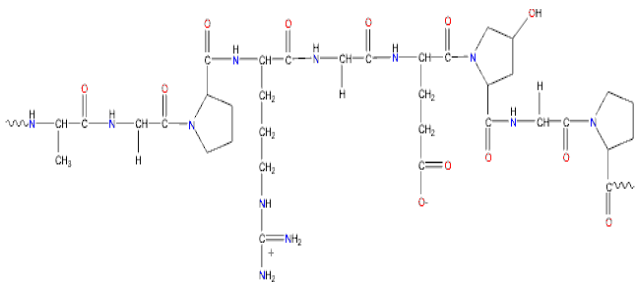

Figure 1: The Capital Costs of the Base Case VRB.

Experimental

Materials

Gelatin (185 Bloom; Type A, pharmaceutical grade) was collected from the Opsonin Pharma Limited, Barishal, Bangladesh. The monomer BDDA was purchased from E. Merck, Germany, and acetone from BDH Chemicals Limited, England. Methanol was purchased from E. Merck, Germany. The synthetic polymer PVA (Molecular Weight: 72000) was purchased from Fluka Chemie AGCH-9470 Buchs.

Methods

Preparation of film: Gelatin was dissolved in hot water to form solution. Poly vinyl alcohol (PVA) was also dissolved in hot water with constant stirring. Then these two solutions were mixed. The mixture was continuously stirred with the help of magnetic stirrer to form homogeneous mixture and heated for about one and half an hour. The solution was then cast on to the silicon paper covered glass plate to form film. The solution layer was maintained into a thickness of 4 mm on the glass plate. The solution was dried into films at room temperature for 48 hours.

The dried films were then peeled from the silicon cloth and cut with a scissor into small pieces of length 70 mm and width 10 mm. Thickness was measured by slide calipers and that was 1.5 mm on an average. These samples were stored in laminated polythene bag and kept in desiccators at room temperature prior testing. These samples were irradiated under γ (gamma)-radiation with different doses (total dose) like 0.5, 1.0, 1.5, 2.5 and 5.0 kGy.

Preparation of soaking formulation using 1,4-Butanediol diacrylate (BDDA): One soaking formulation was prepared with BDDA (3%) in methanol.

Treatment of films: Gelatin and Gelatin/PVA bio blended Films were irradiated under γ-radiation at different doses of gamma radiation like 0.5, 1.0, 1.5, 2.5 and 5.0 kGy using γ-ray from ^{60}Co. The Films were then subjected to various characterizations.

Characterization of Gelatin/PVA bioblended film: The films were exposed at room temperature for well grafting for about 24 hrs. After this tensile strength (TS), Elongation at break (Eb), Scanning Electron Microscopy (SEM), and FTIR were measured.

Treatment of films with soaking formulation: Gelatin and Gelatin/PVA bioblend film of the composition (95:5) was soaked in 3% BDDA at 3 minutes soaking time. After soaking, these films were irradiated under γ- radiation at different doses of gamma radiation like 0.5, 1.0, 1.5, 2.5 and 5.0 kGy using γ-ray from ^{60}Co. The films were then subjected to various characterizations.

An electromagnetic wave, a gamma ray is similar to ordinary visible light but differs in energy or wavelength. Sunlight consists of a mixture of electromagnetic rays of various wavelengths, from the longest, infrared, through red, orange, yellow, green, blue, indigo, and violet, to the shortest in wavelength, ultraviolet. A gamma rays wavelength is far shorter than ultraviolet (i.e., it is far higher in energy). Gamma rays are produced following spontaneous decay of radioactive materials, such as cobalt-60 and cesium-137. A cobalt-60 gamma ray can penetrate deeply into the human body, so it has been widely used for cancer radiotherapy.

Gamma radiation has more energy and therefore it is possible for the electrons to be discharged. This results in the creation of electrically charged particles, which are called ions. The amount of energy deposited in the product is referred to as the "absorbed dose" (1 kilo Gray=1 kilojoules/kg) (Figure 2).

If we relate it to heat, 10 kGy is equal to the amount of energy required to raise the temperature of 1 kg of water by 2.4°C.

Property measurement

Tensile properties: Tensile properties; tensile strength (TS) and elongation at break (Eb) of the cured films are measured with Universal Testing Machine (INSTRON, model 1011, UK). The load capacity is 500 N, efficiency is within ± 1%. The crosshead speed is 10 mm/min. Gauze length is 30 mm. Following equations are used to measure the tensile properties.

$$\text{Tensile strength, TS}\ (\text{MPa}) = \frac{\text{Load}\ (\text{N})}{\text{Thickness}\ (\text{mm}) \times \text{Width}\ (\text{mm})}$$

$$\text{Elongation at break, Eb}\ (\%) = \frac{\text{Displacement at break}}{\text{Gauze length}} \times 100$$

FTIR analysis: Pure gelatin film, pure PVA film and a blend (95% gelatin+5% PVA) was characterized by FT-IR.

Morphological characteristics: The surface morphology of gelatin, PVA and their blends were determined by Scanning Electron Microscopy (SEM).

Results and Discussion

Generally Gelatin is insoluble in cold water. So, Gelatin was dissolved in hot water. Gelatin was blended with poly (vinyl alcohol), a biodegradable synthetic polymer, in order to improve physico-mechanical and thermal properties in the films.

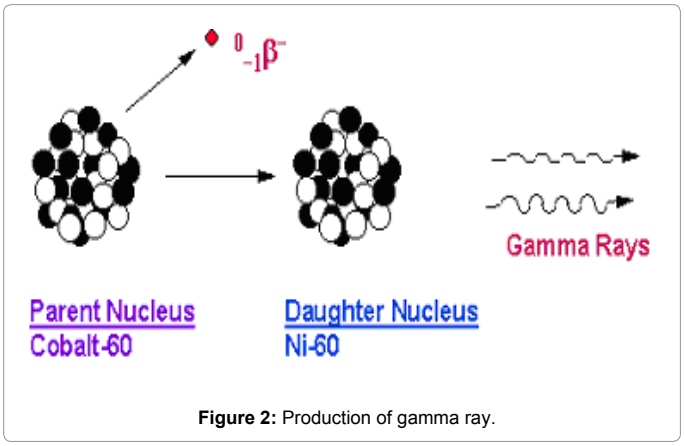

Figure 2: Production of gamma ray.

Preparation and chractarization of Gelatine/PVA blend

Gelatin containing 5, 10 and 15% PVA solution and PVA containing 5, 10, 15 and 20% gelatin solution were blended for preparing Film. These solutions were blended in hot water for about one and half an hour to produce homogenous solution at the end of the process. During cooling, the solution was transformed into semi gel and then was casted on to silicon paper covered glass plate for Film formation.

γ-Radiation process and optimization of γ-radiation dose

Different concentrations of PVA blended Gelatin were taken for grafting under γ-radiation. Better grafting means better cross-linking of polymer. We observe the effect of concentration of polymers and the effect of radiation doses. Various physico-mechanical and thermal properties like tensile strength (TS), elongation at break (Eb), FTIR, and SEM (Scanning Electron Microscope) of films were observed. For untreated (virgin) Film, radiation doses were optimized for such types of properties.

Mechanical properties of untreated and treated film

Four different blends were prepared from various concentrations of gelatin/PVA solutions. When blends were prepared by mixing gelatin and PVA water solution, a homogeneous water solution was produced, thus showing compatibility of the two components in the solvent, whereas cast films appeared homogeneous only for a limited amount (20%) of one component into the other. Thus, in blends with the same amount of PVA and gelatin, phase separation and opacity were evident. These were impossible to handle. So we investigated the physico-mechanical properties of films of above mentioned compositions.

Optimization of grafting condition with extent of physic-mechanical properties

Tensile strength (TS): Tensile strength (TS) is very important in selecting diverse application of polymer. The results of TS values of the not radiated Films (gelatin and PVA based) were plotted in Figure 3 for 0%, 5%, 10% and 15% (GP1, GP2, GP3 and GP4) PVA containing gelatin Films. The TS values of irradiated Films were plotted in Figure 4 against total dose (γ-radiation dose). From the Figure 3 it was observed that with the loading of PVA into gelatin the TS (tensile strength) of the base polymer were significantly decreased. But, from Figure 4 it was seen that, due to incorporating radiation the TS values were improved up to some radiation dose and then again decreased. The highest TS for blends were observed for 5% PVA containing Gelatin Film at 0.5 kGy dose (51 MPa). In case of pure Gelatin Film TS values was also increased with the increase of radiation doses and TS value attained maximum at 0.5 kGy (total dose) and then decreased with increasing radiation doses. Higher γ-radiation dose might have caused degradation of the polymer and the Film became hard and brittle whilst at lower doses cross linking might have dominated over chain seasoning.

In case of irradiated Film, TS values were reached a maximum up to approximately 0.5, 1.5 kGy (radiation dose) and then decreased for further increasing of radiation intensity as well as Gelatin concentration. When the Gelatin Film subjected to the radiation, hydroxyl group from Gelatin radicals were initiated to form cross linked network. So, TS value increases with radiation, but higher radiation doses caused degradation due to the breaking of the polymer chains. So, at higher radiation doses TS decreased. From the figure it is clear that TS value of gamma treated Film is higher than that of untreated Film.

Tensile Strength (TS) of different formulations change with γ-irradiation dose. At 0.5 kGy tensile strength of GP1, GP2, GP3, and GP4 is 56.65, 51.67, 32.11, and 28.45 respectively. But tensile strength of non-irradiated GP1, GP2, GP3, and GP4 is 41.34, 34.94, 29.19, and 11.54 respectively.

Elongation at break (Eb): Elongation is an important mechanical property in the application of polymer. The results of elongation at break (%) of the not radiated Films (gelatin and PVA based) were plotted in Figure 5 for 0%, 5%, 10% and 15% (GP1, GP2, GP3 and GP4)

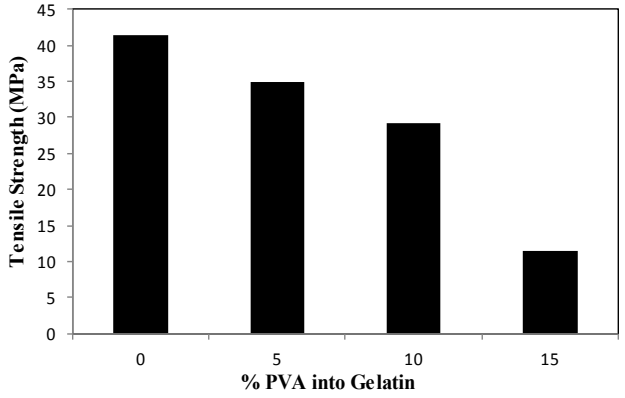

Figure 3: Tensile Strength of PVA Containing Gelatin Film.

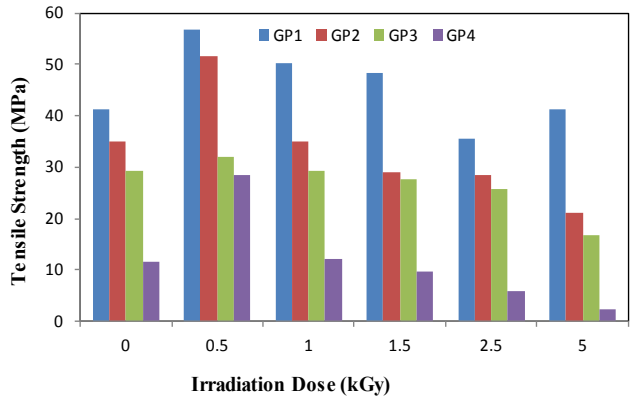

Figure 4: Tensile Strength of Gelatin-PVA Film (Gelatin Based) Against Different Gamma radiation Dose (kGy).

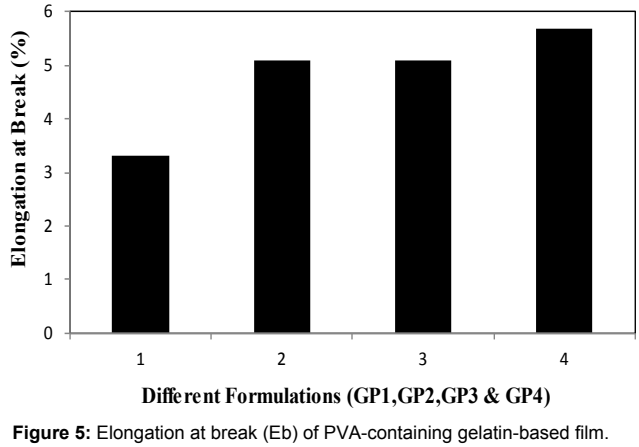

Figure 5: Elongation at break (Eb) of PVA-containing gelatin-based film.

PVA containing gelatin films. The Eb (%) values of irradiated films were plotted against total dose (γ-radiation dose) in Figure 6. It is observed that Eb value increases for blend films drastically due to incorporating PVA. This is due to the increasing concentration of highly flexible PVA into the blend films. The highest Eb is found to be 5.6% for the film obtained from GP4 formulation (85% gelatin+15% PVA). The Eb values of irradiated films are plotted (Figure 6) against gamma irradiation dose as a function of formulation. It is found that Eb values decrease with the increase of irradiation dose for all formulations.

In the case of blend films, the maximum Eb of 4.8% is observed for the GP2 formulation at 0.5 kGy dose, followed by 3.8% and 4.2% for GP3 and GP4 formulation, respectively, at the same irradiation dose. Elongation at break (Eb) changes with gamma irradiation dose at 0.5 kGy are shown in Table 1. It is clear that the Eb of gamma treated film is lower than that of untreated film [12].

Elongation at break (%) changes with γ-irradiation dose. At 0.5 kGy elongation at break (%) of non-irradiated GP1, GP2, GP3, and GP4 is 3.2, 5.1, 5.09, and 5.67 respectively. But after irradiation elongation at break (%) of GP1, GP2, GP3, and GP4 is 3.16, 4.79, 3.83, and 4.23 respectively.

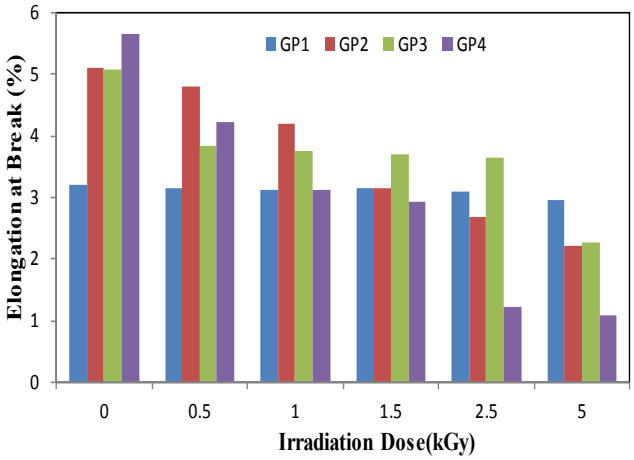

Figure 6: Elongation at break (Eb) of gelatin-based PVA film against different gamma irradiation dose (kGy).

Fourier Transformed Infrared Spectroscopy (FTIR) analysis

FTIR is of importance to study the molecular structure. The width and intensity of spectral bands as well as position of peaks are all sensitive to environmental changes and to conformations of macromolecule on molecular level. Intermolecular interactions occur when two polymers are compatible. So the FTIR spectra of the blends are different from those of the pure polymer, which is advantageous to study the extent of compatibility of the blend polymers. FTIR spectrophotometer has also been found to be a valuable tool in studying graft copolymerization reactions. Figures 7, 8 and 9 shows the infrared spectra for the films of pure gelatin, pure PVA and the irradiated blend in the wave number range of 2400-500 cm^{-1}.

The FTIR spectra of untreated pure gelatin shown in Figure 7. The most distinctive spectral features for the protein were the strong amide I and II bands centered at approximately at 1640 and 1550 cm^{-1}, respectively. The amide I absorption was primarily due to the stretching vibration of the C=O bond and the amide II band was due to the coupling of the bending of the -NH bond and the stretching of the C-N bond. The FTIR spectra of untreated pure PVA shown in Figure 8. The peaks at 1088 cm^{-1} indicated the C-O stretch of secondary alcoholic groups.

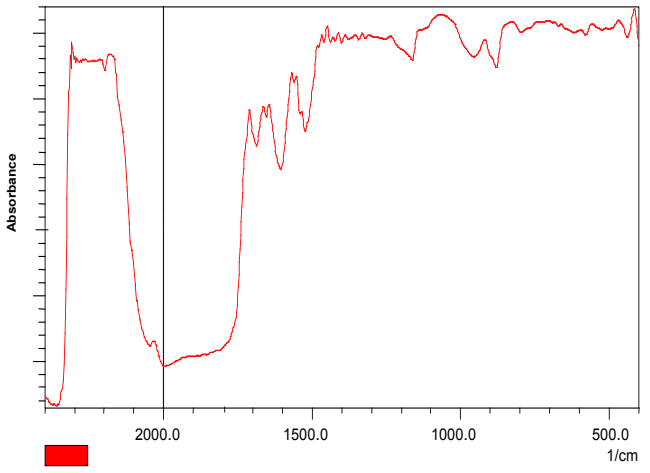

Figure 7: FTIR Spectrum of Untreated Pure Gelatin.

The FTIR spectrum of irradiated blend (95% Gelatin+5% PVA) was given in Figure 9. The grafted product does not show any characteristic peak corresponding to carbonyl group and amino group indicating the crosslinking through these groups.

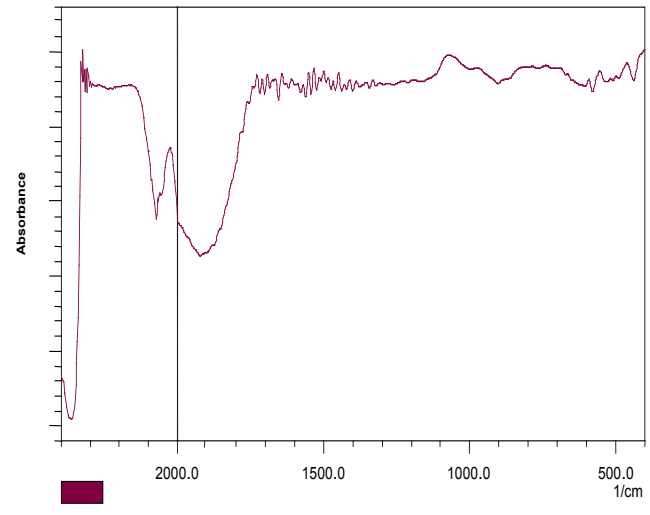

Figure 8: FTIR Spectrum of Untreated Pure PVA.

Scanning Electron Microscopy (SEM)

Scanning electron microscopic (SEM) image of untreated pure gelatin, pure PVA and an irradiated blend (95% Gelatine+5% PVA) were shown in Figures 10, 11 and 12. In order to study surface morphology SEM study was undertaken. In Figure 10 some unbound micro granules was observed. The SEM of PVA showed better film forming property than gelatin. Figure 12 indicating some type of interaction between gelatin and PVA due to irradiation. Crosslinking and chain scission occurred when polymers were exposed to gamma irradiation [17]. Polysaccharides and other natural polymers generally degrade by breaking the glycosidic linkage under gamma radiation [17].

Composition (% w/w)		
Formulation	**Gelatin (%)**	**PVA (%)**
GP1	100	00
GP2	95	05
GP3	90	10
GP4	85	15

Table 1: Composition of different blending formulations (% w/w).

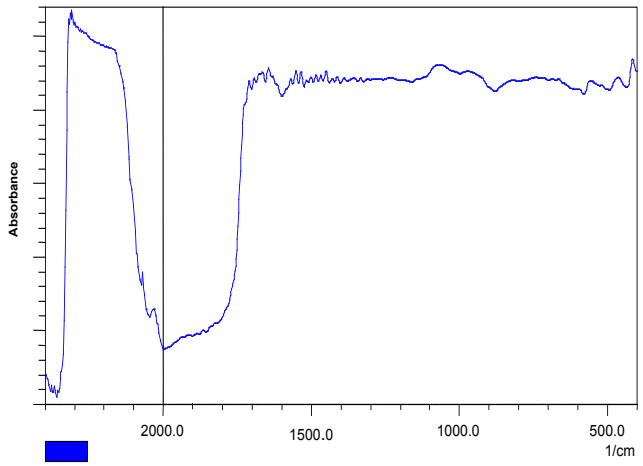

Figure 9: FTIR Spectrum of Radiated Blend (95% gelatin+5% PVA).

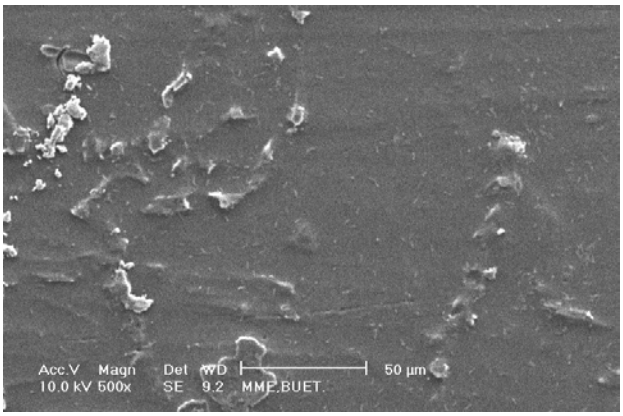

Figure 10: A SEM Micrograph of Untreated Gelatin Film.

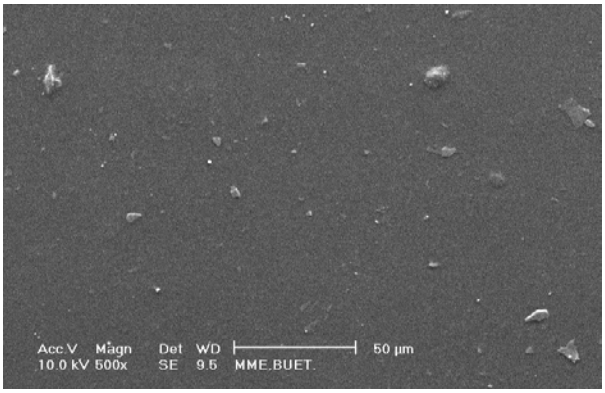

Figure 11: A SEM Micrograph of Untreated PVA Film.

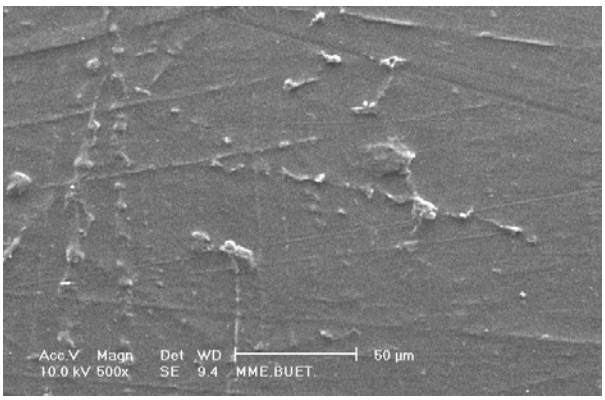

Figure 12: A SEM Micrograph of Radiated Film (95% Gelatin+5% PVA).

Conclusion

The mechanical and morphological properties of irradiated PVA mixed gelatin films indicated higher compared with the non-irradiated films. It was found that 95% gelatin+5% PVA film exhibited the highest tensile strength (TS) value at 0.5 kGy gamma radiation (51 MPa), which was 46% higher than that of non-irradiated films. Elongation at break (Eb) changes with gamma irradiation dose. The Eb of gamma treated film is lower than that of untreated film. The FTIR Spectrum of Radiated Blend (95% gelatin+5% PVA) blend shows that the grafted product does not show any characteristic peak. The SEM (Scanning Electron Microscopy) images indicate some sorts of interaction between gelatin and PVA due to irradiation. The ultimate target concluded that the enhanced property of PVA mixed gelatin films is obtained, which may be suitable for bio-medical applications.

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