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SYNTHESIS AND CHARACTERIZATION OF BIODEGRADABLE POLYVINYL ALCOHOL/ GELATIN POLYMER BLEND FILM BASED ON GAMMA RADIATION

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Abstract:

In this study, Polyvinyl alcohol (PVA)/ gelatin polymer blend were synthesized and mixed with citric acid as a plasticizer then exposed to two different doses of gamma irradiation. The optical and morphological properties, have been investigated by using the Scanning electron microscope (SEM), Fourier transformer infrared spectroscopy (FTIR), UV-visible absorption and swelling degree measurements. The IR spectrum shows a strong chemical interaction between PVA and gelatin molecules with the formation of new peaks in the range 1227-1364 cm^{-1}. SEM and the UV–visible absorption measurements support the idea of improved miscibility after exposing the PVA/ gelatin blend to gamma irradiation. Swelling degree results of the blend indicated sufficient water holding capacity.

Key words: *PVA/Gelatin blends, Gamma irradiation, Films, Characterization.*

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INTRODUCTION:

Polymeric materials have attracted scientific and technological researchers because of their widespread applications. This is mainly due to the light weight, good mechanical strength, and optical properties, which make them multifunctional materials. Moreover, these polymers are traditionally considered excellent host materials for blending[1]. In recent years, polymer blends and composites have been subjects of interest for both theoretical and experimental studies because of certain physical and chemical properties needed for specific applications that may be obtained by blending. It has been observed that polymer blending has a significant effect on the physical properties, including optical, thermal, and electrical properties. These changes in physical properties depend on the chemical nature of the guest material and the way in which it interacts with the host polymer. Systematic investigations reported in the literature show that many polymers have two coexistent phases, crystalline and amorphous. When such polymers are blended with a suitable material, they may interact either in the amorphous fraction or in the crystalline fraction of the polymers, and in both cases, the polymeric properties will be altered. Hence, complete information about the effects of additives on a specific polymer helps in tailoring that polymer for a particular application [2,3]. Poly (vinyl alcohol) (PVA) has been used for more than 40 years because of its unique chemical and physical properties [4]. These properties come from its hydroxyl groups. The hydrogen bonding between hydroxyl groups plays an important role in the properties of PVA, such as its high-water solubility, wide crystallinity range, and high crystal modulus[5]. The important features of semi-crystalline PVA are the presence of crystalline and amorphous regions and its physical properties, which result from the crystal–amorphous interfacial effect. These two regions are well separated by portions of an intermediate degree of ordering, and this enhances the macromolecules, producing several crystalline and amorphous phases [6]. PVA is normally a poor electrical conductor; it can become conductive upon blending with some polymer. The poor conducting nature of PVA is thought to be due to the high physical interactions between polymer chains via hydrogen bonding with hydroxyl groups as well as the complex formation [2,3,6-9]. Gelatin is a well-known material widely used in biomedical applications [10-13]. There are various studies on the compatibility of gelatin-based blends and composite films, but still the compatibility of PVA/ gelatin blend films is an important parameter from the point of view of the behavior of the two polymers in the blend. In view of this, it is very important to note that the blending modifies the structure of the polymer and hence its properties because the changes in the polymer properties mainly depend on both the polymers and the way in which they interact with each other.

EXPERIMENTAL:

Materials

PVA used in this work was obtained in a powder form C.R.C Fine Chemicals, Ltd.(Italy), with a molecular weight of 450,000 g/mol and degree of polymerization of 1750-50. The gelatin used in this work is type B derived from bovine skin, with Bloom number 50-300 and presents an iso-electric point between 4.7 and 6, was purchased from Fisher scientific Fine Chemicals, Ltd (Germany) and used without further purification. Canada. Citric acid used in this work is white powder($C_6H_8O_7.H_2O$), with molecular weight of 210.14 g/mol, assay 99.5-100.5%, was obtained from PRS Panreac Company, (Spain). HCl used, which is of analytical grade, purchased from Aldrich. The water used was distilled and de-ionized water. All reagents, which were all of analytical grade, were used as received.

Preparation of PVA/ gelatin polymer blend films

Films of PVA/Gel blends were prepared by casting solution technique [14]. Aqueous 10 wt.% PVA/Gelatin solutions were prepared by dissolving 4 g PVA and 6 g Gelatin in 125 ml water and refluxing these at 90 OC for 30 min. Then (0.5ml of Citric acid 0.1N) was mixed [15], and the mixture was stirred for 90 min before casting into a plexi glass plate placed on a leveled flat surface. After the blends were allowed to dry at 50OC in an oven for 12 h, the fully dried membranes were peeled away from the glass plate, then they were heated in a thermosetting oven at 95OC for 1 h to induce crosslinking reaction.

Characterization

The scanning electron microscope (SEM) was employed with the scanning electron microscope of JEOL-JSM-5500 LV (Japan). The IR spectra were recorded over the range (400 – 4000 cm-1) at resolution 4 cm-1 by using Fourier transform infrared spectrometry(FT-IR-6300)-Japan,. Ultravilote/visible spectroscopy,(UV/VIS) spectrometer (Jasco/v-560) made in Japan, was used for scanning the absorption spectra in the range 200 nm to 900 nm wavelengths. Swelling study was conducted on the (PVA/Gelatin) as a function of time in which a dry weight of insoluble polymer blend of (PVA/Gelatin) (W1) was immersed in distilled water,

at 25°C for different intervals of time durations up to 24hrs. After each time interval, the sample was withdrawn and blotted on filter paper to remove excess water and weighed (Wt.), in which the degree of swelling is calculated according to the following equation [16]:

Degree of swelling (%) = [(Wt - W1)/ W1] X100

Irradiation to the required doses was carried out in a 60Co gamma cell (made in India) at the National Center for Radiation research and Technology, Cario, Egypt. Irradiation was carried out under atmosphere at a dose rate 6.92 kGy/h.

Results and discussion

Structure Morphology by SEM

Polymer blend exhibit a solid-phase separation producing circular domains with light edges and dark core whose proportions and dimensions are dependent on the blend composition as shown in *Fig*. 1. The observed dark and light regions in SEM images are regarded as the PVA and gelatin phases respectively [17]. The average radius circles were 20 µm for image A (25/75), 15 µm for image B (50/50) and 5 µm for image C (75/25) of (PVA/Gelatin) film. It noted that the radius was decreased markedly with decreasing Gelatin ratio. Also, the surface morphology of (75/25) of (PVA/Gelatin) film exhibit a few cracks of different lengths.

When the polymer blend ratios of (PVA/Gelatin) films were irradiated with different doses of gamma irradiation, the separated domains lost its circular shape. It was observed that the more flaky structure with globules appeared at the dose of 5 and 20KGy (see *Fig*. 2-7). These globules have small size distribution in case of the applied dose 20KGy of gamma irradiation to irradiated (PVA/Gelatin) films, and the size is markedly decreased as the irradiation dose increase [18]. Also, by increasing irradiation dose from 5 to 20KGy leads to more degradable of gelatin in the blend composition, which cause appearing cracking in the investigated polymer blend ratios. Generally, it can be seen that upon irradiation treatment, significant indication to the miscibility *enhancement.*

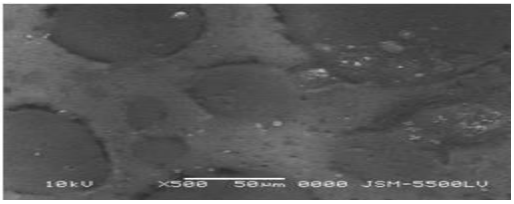

***Figure* 1-A**. SEM of unirradiated polymer blend films ratio (25/75) of (PVA/Gelatin).

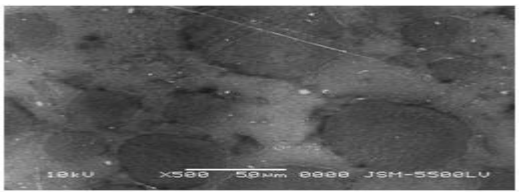

***Figure* 1-B.** SEM of unirradiated polymer blend ratio (50/50) of (PVA/Gelatin) film.

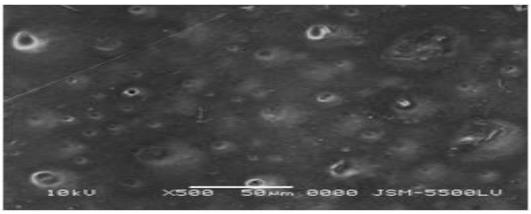

***Figure* 1-C.** SEM of unirradiated polymer blend ratio (75/25) of (PVA/Gelatin) film.

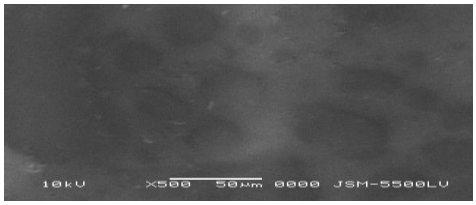

***Figure* 2.** SEM of irradiated polymer blend ratio (25/75) of (PVA/Gelatin) film at 5KGy.

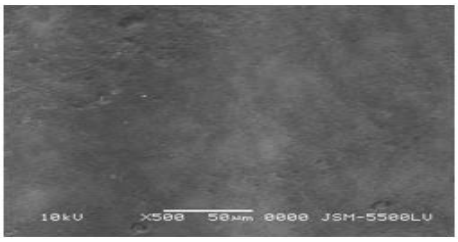

***Figure* 3.** SEM of irradiated polymer blend ratio (25/75) of (PVA/Gelatin) film at 20KGy.

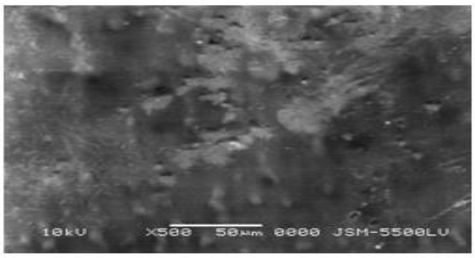

***Figure* 4.** SEM of irradiated polymer blend ratio (50/50) of (PVA/Gelatin) film at 5KGy.

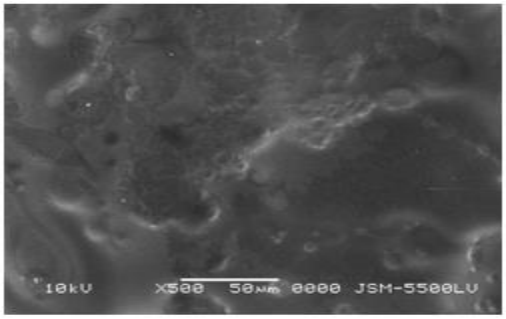

***Figure* 5.** SEM of irradiated polymer blend ratio (50/50) of (PVA/Gelatin) film at 20KGy.

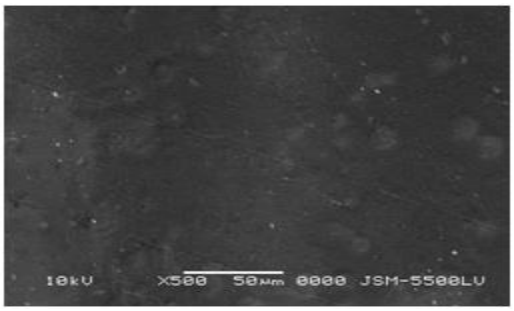

***Figure* 6.** SEM of irradiated polymer blend ratio (75/25) of (PVA/Gelatin) film at 5KGy.

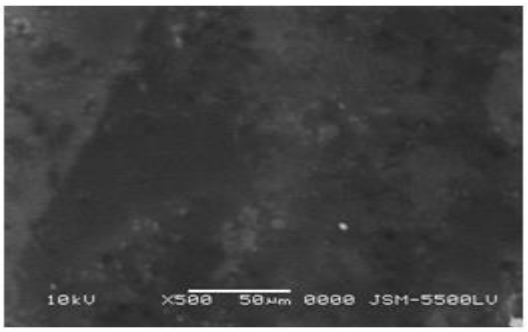

***Figure* 7.** SEM of irradiated polymer blend ratio (75/25) at 20KGy.

IR Spectroscopy Analysis

Carefully examination of data in *Fig.* 8, reveals that the peaks of Gelatin at 3500-3330 cm^{-1} due to NH stretching of secondary amide C=O stretching at 1680 cm^{-1}, NH bending between 1550 cm^{-1} and 1500 cm^{-1}, C─O─C finger print around 554 cm^{-1} and 533 cm^{-1}. On the other hand, the listed peaks of PVA, showed abroad peak around 3500-3400 cm^{-1} indicating stretching of hydroxyl groups and peaks between 2940 cm^{-1} and 2800 cm^{-1} due to CH_2 asymmetric stretching, while, the peak at the range 2300-2000 cm^{-1} is attributed to combination frequency of (CH+C≡C) and the peak at 1093 cm^{-1} assigned to C─O─C stretching vibration. The spectra of the unirradiated polymer blend of (PVA/Gelatin) films *Fig.* 8 showed a peak in the range 3330-3340 cm^{-1} assigned to stretching vibration of hydroxyl group with strong hydrogen bonding as intra-and/or intertype [18-21]. The shoulder absorption peak at 3600 cm^{-1} is associated with free hydrogen bonding O─H stretching [18]. Also, it can be observed from the spectra of the unirradiated polymer blend of (PVA/Gelatin) films that the peak of gelatin at 1680 cm^{-1} shifted to1729-1745 cm^{-1} *Fig.* 8, indicating the formation of an esterified product [15,22,18,23]. The peaks at 1460 cm^{-1} and 1100 cm^{-1} are assigned to NH2 bending vibration and C─O─C stretching vibration respectively [24-27]. Meanwhile, a small shoulder peak at 541 cm-1 is attributed to C─O─C finger print [28]. The peak 2920 cm^{-1} *Fig.* 8, indicates the presence of CH_2 symmetric stretching [19,20], while the NH3 stretching vibration appeared at 2374 cm^{-1}[24].

Different remarkable changes were notice here under different doses of gamma irradiation as shown in *Fig.* 9-10. The first is the feature in the O—H stretching region 3600 cm^{-1} peak becomes sharper as irradiation dose increases. This may be due to breaking of hydrogen bonds as a result of irradiation treatment which results in formation of non-hydrogen bonding O—H groups and hence the intensity of the peak at 3600 cm^{-1} was increased as the increasing irradiation dose [18]. The shape of FT-IR absorption peak in the range 3330-3340 cm^{-1} in the irradiated polymer blend of (PVA/Gelatin) films is changed and shifted to lower frequency side [18]. Secondly asymmetric stretching at 2908 cm^{-1} is absent in presence of higher irradiation dose (20KGy) which may be attributed to breaking of hydrogen bond by irradiation [23] (see *Fig.* 10). Thirdly, in contrast a new broad band in the range 1227-1364 cm^{-1} is appeared in the irradiated ratios mainly due to extension of the C─N group [29,30]. Fourthly, the C=O stretching vibration intensity 1729 cm^{-1} was increased with increasing irradiation dose [18]. It is noteworthy that the free radical arising from the interaction of the ionizing radiation and the (PVA/Gelatin) polymer blend reacts with O—H groups giving rise to the formation of ether bonds between the polymeric chains, leading to the crosslinking and in solubilization of (PVA/Gelatin) polymer blend. This is an evidence for formation C─N and C─C at 1227 cm^{-1} and 855 cm^{-1} respectively after irradiation [18].

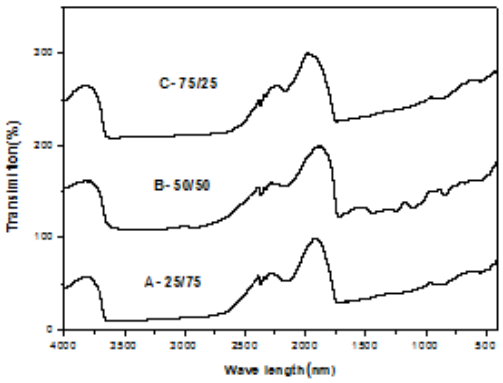

***Figure* 8.** IR Spectra of unirriadiated polymer blend ratios of (PVA/Gelatin).

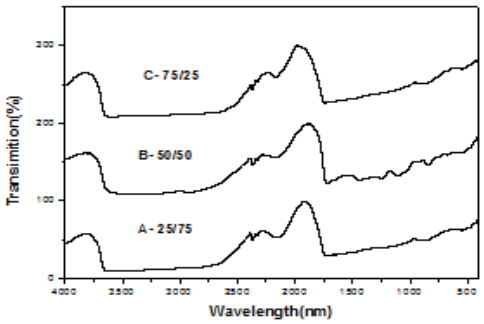

***Figure* 9.** IR Spectra of irradiated polymer blend ratios of (PVA/Gelatin) at 5kGy.

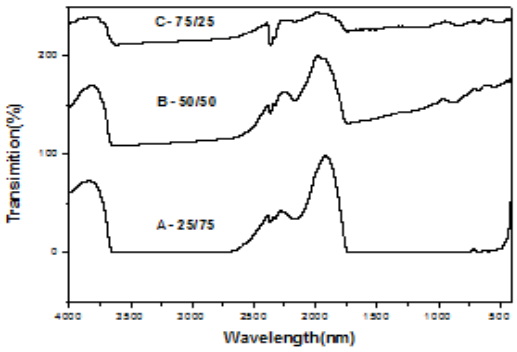

***Figure* 10.** IR Spectra of irriadiated polymer blend ratios of (PVA/Gelatin) at 20kGy.

UV-visible spectroscopy Analysis

Fig. 11 observe a gradual decrease in the absorption of spectral range 190-400 nm with appearance of absorption shoulder peaks at 225 nm and 290 nm followed with nearly zero absorbance intensity in the wavelength range 400-900 nm of the unirradiated ratios of (PVA/Gelatin) polymer blend films. The band observed at 244 nm with higher intensity 4.92nm can be attributed to amino acids in gelatin which assigned to π— π * transition.[31] While, the band at (290 nm) with lower intensity 2.92nm can be attributed to the high energy absorption in the UV region and may assigned to π— π * transition which comes from unsaturated bands, mainly C=O and or C=C, which are probably due to carbonyl groups as a result of residual acetate groups remaining after the manufacture of PVA from hydrolysis of polyvinyl acetate or oxidation during manufacturing and processing [32]. It is worthy to mention that the increasing in PVA content in polymer blend of (PVA/Gelatin) increases the miscibility and hence the transparency. This behavior considered as evidence for increasing intensity of peaks [33].

Generally, from obtained results a significant increase in the optical density of irradiated (PVA/Gelatin) polymer blend with increasing PVA content which might be attributed to the decrease of gelatin content after exposure to different doses of gamma radiation (5KGy and 20KGy) (see *Fig.*12 and 13). Accordingly, the absorption peaks corresponding to the PVA/Gelatin (290 nm), were found to sensitive to blend component percent and irradiation dose in such a way that the absorption peaks intensities increased by increasing either the PVA content and/or irradiation dose. On other hand, it was obvious that the absorption peak at (225 nm) assigned to amino acids in gelatin was increased as increasing either PVA percent and/or irradiation dose. The lower values of absorption peaks were observed for irradiated ratio (75/25) of PVA/Gelatin film at irradiated doses 5 and 20KGy respectively.

It worth to mention that the increasing in irradiation dose was found to improve the transparency of polymer blend, on the basis of reflectance measurements, indicating improvement in miscibility. In this regard, the highest improvement in miscibility was observed in the case PVA/Gelatin (75/25) blend in which transparency was increased. The intensity of UV absorbance of bands 225 and 290 nm are in accordance with these findings, in which PVA/Gelatin (75/25) blend irradiated to 20KGy gives higher absorbance than the same ratio irradiated at 5KGy [33].

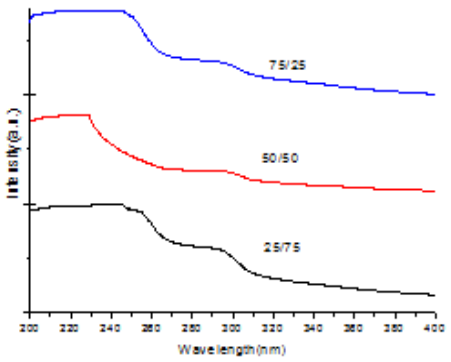

***Figure* 11.** UV-visible spectra of unirradiated polymer blend ratios of (PVA/Gelatin).

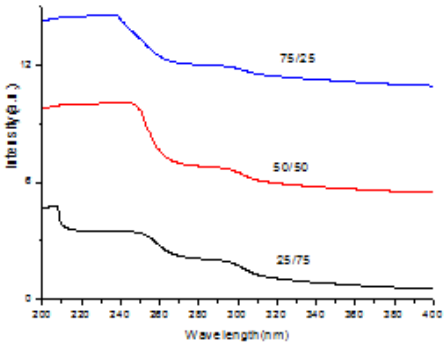

***Figure* 12.** UV-visible spectra of irradiated polymer blend ratios of (PVA/Gelatin) at 5kGy.

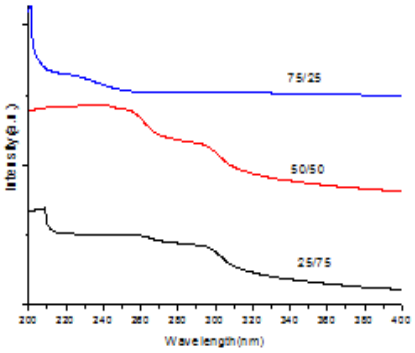

***Figure* 13.** UV-visible spectra of irradiated polymer blend ratios of (PVA/Gelatin) at 20kGy.

Swelling degree:

The degree of swelling ratios of unirradiated polymer blend of (PVA/ Gelatin) film at room temperature is plotted against time in *Fig.* 14. The data reveal that, the swelling degree percentages gradually decreases with increasing PVA content in the polymer blend films. Also, since gelatin is more hydrophilic than PVA so that, the swelling degree percentages increased with an increase in the molar ratio of hydrophilic groups of gelatin component. Also, from the FTIR results of the polymer blend, it is clear that the whole carboxylic group of the gelatin has been esterified but the free amino groups are present. From this fact it can be hypothesized that these free amino groups play an important role in water uptake because of their hydrophilic nature [22].

It was observed from *Fig.* 14 that the unirradiated polymer blend film were observed to swell rapidly during initial times for (25/75) (PVA/Gelatin) up to 550%, 300% swelling was observed for the ratio (50/50) of (PVA/Gelatin), and 240% for (75/25) (PVA/Gelatin) after 6,4 and 2hrs respectively. The swelling degree percentages (%) start to decrease gradually to be (425%) after 8 hrs, of immersion the unirradiated ratio (25/75). The ability of blend ratios (50/50) and (75/25) for swelling began to decrease after 6 and 4 hrs of dipping in distilled water (225% and 178%) respectively. The obtained results, may be attributed to the esterfication of PVA in the presence of citric acid [34].

The obtained data (see *Fig.* 15 and 16), it is obvious, that the swelling degree percentages of irradiated polymer blend of (PVA/Gelatin) films gradually decreases with increasing of irradiation dose, indicating an increase in crosslink density of irradiated polymer blend films, which make polymer chain more rigid and compact [35]. This behavior reduces the average chain length between cross-links, restricting chain motion and extension. Volumetric expansion of polymeric network decreases as a function of increasing crosslink density. It was also observed that increasing gelatin content into polymer blends increases the swelling ratios, and this is due to the increment in PVA hydrophilicity [36].

It can be seen that the maximum swelling degree percentages increases in presence of the applied dose (5KGy) of gamma irradiation, then it begins to decrease slightly after saturation time (24 hrs). The maximum swelling degree percentage of irradiated ratio (25/75) in distilled water after 6 hrs was 887% while, swelling degree percentage for the irradiated ratios (50/50), (75/25) were 720% and 360% after 8 and 2 hrs respectively as shown in *Fig.* 15. The

swelling degree percentages values of irradiated polymer blend ratios (25/75), (50/50) and (75/25) of (PVA/Gelatin) films at (20KGy) becomes a maximum (500%, 445% and 342%) after 4, 2 and 6 hrs respectively (see *Fig.* 16).

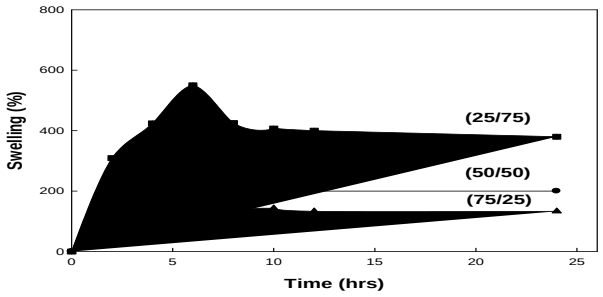

***Figure* 14.** Swelling-time dependency of unirradiated polymer blend ratios of (PVA/Gelatin) in distilled water.

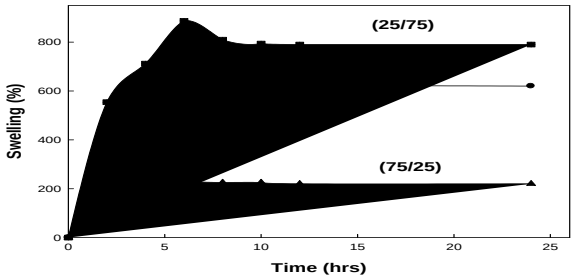

***Figure* 15.** Swelling-time dependency of irradiated polymer blend ratios of (PVA/Gelatin) in distilled water at 5kGy.

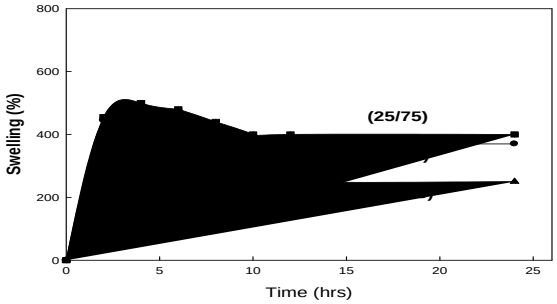

***Figure* 16.** Swelling-time dependency of irradiated polymer blend of (PVA/Gelatin) in distilled water at 20kGy.

CONCLUSION:

In this work, PVA/Gelatin blend films, synthesized by casting solution technique, were successfully prepared by gamma irradiation to be used as biodegradable materials. The recorded investigation may lead to the conclusion that exposure to gamma irradiation can be used as a technique to improve the miscibility of polymer blend. The results of IR spectra showed that crosslinking occurred, after irradiation. The results of SEM and UV- spectra partially confirmed the FT-IR analyses. It was also observed that increasing gelatin content into polymer blends increases the swelling ratios, and this is due to the increment in PVA hydrophilicity.

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