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Preparation of Polyvinyl Pyrrolidone-Based Hydrogels by Radiation-Induced Crosslinking with Potential Application as Wound Dressing

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Polyvinyl pyrrolidone/polyethylene glycol hydrogels (PVP/PEG) and PVP/PEG/Starch were prepared by irradiating the mixtures of aqueous solutions of PVP, PEG and starch with electron beam at different doses. Their properties were evaluated to identify their usability in wound dressing applications. The physical properties of the prepared hydrogels, such as gel content, swelling, water content and degree of water evaporation with varying composition and irradiation dose were examined to evaluate the usefulness of the hydrogels for wound dressing. The gel content increases with increasing PVP concentration due to increased crosslink density, and decreases with increasing the PEG concentration. PEG seems to act not only as plasticizer but also to modify the gel properties as gelation% and maximum swelling. Mechanical experiments were conducted for both PVP/PEG and PVP/PEG/Starch. The adding of PEG and starch to PVP significantly improves elongation and tensile strength of prepared hydrogels, respectively. The crystallinity of both prepared hydrogels was investigated with varying their components, XRD studies indicated that the crystallinity in the gel was mainly due to PVP and mainly decreased with enhanced starch content. The prepared hydrogels had sufficient strength to be used as wound dressing and could be considered as a good barrier against microbes.

Keywords: Hydrogels, irradiation, polyethylene glycol, polyvinyl pyrrolidone, starch, wound dressing

1. Introduction

Hydrogels are three-dimensional hydrophilic networks capable of imbibing large amounts of water, which have been used widely in the fields of biomedicine and pharmacy (1,2), such as an interface between bone and an implant (3), wound dressings (4), contact lenses (5), blood contact materials (6) and in-controlled release applications for delivery of enzymes, hormones, contraceptives, anticoagulant, etc. (7). Synthetic polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and polyethylene oxide hydrogels have been studied widespread but their properties need to be improved further for special applications (8,9). Hydrogels of natural polymers, especially polysaccharides, have been used recently because of their unique advantages. Polysaccharides are, in general, non-toxic, biocompatible, biodegradable, and abundant (10,11). However if the polysaccharide dissolves in water, it cannot form stable hydrogel. One effective method to avoid these limitations is to combine them into a synthesized polymer blend hydrogels, which is becoming a subject of academic as well as of industrial interest.

Ionizing radiation has long been recognized as a suitable tool for the formation of hydrogels. Easy process control, possibility of joining hydrogel formation and sterilization in one technological step, no necessity to add any initiators, crosslinkers, etc., having no waste, and relatively low running costs, are advantages of ionizing radiation. These advantages make irradiation a method of choice in the synthesis of hydrogels, especially for biomedical use. Radiation production of hydrogel wound dressings (HWDs) started first in Poland at the Technical University of Lodz in 1992. PVP-based dressings, obtained by e-beam irradiation, were commercialized under the registered trademarks KIK-gel® and AQUA-gel®. Since the beginning of 2003, there has been fully automatic HWD production at Instituto de Pesquisas Energeticas e Nucleares (IPEN), Brazil. The dressings, named commercially as Biogel®, were based on PVP and produced by γ-irradiation. In Japan, Takasaki Radiation Chemistry Research Establishment (JAERI) researchers have developed poly(vinyl alcohol) (PVA)-based HWDs crosslinked by e-beams. The National Center for Radiation Research and Technology (NCRRT) Egypt developed the technology of radiation synthesis of HWD in industrial scale. Recently, research has been performed at

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the Bhabha Atomic Research Center (BARC) India for large-scale production of HWDs based on crosslinking of PVA (12). The hydrogel gives a wet environment to wounds which causes faster healing compared with the gauze dressing with a dry environment (9).

PVP has been used successfully as a basic material for the manufacturing of hydrogel wound dressing (13,14). It shows usually good biocompatibility and is widely applied, not only as wound dressing but also as drug delivery system (15). Hilmy et al. reported that the addition of polyethylene glycol to the PVP hydrogel composition could improve the hydrogel barrier against bacteria (16). The combination of natural and synthetic polymers can endow optimal properties for wound repair. Few attempts (17,18) have been made to use starch-based polymers in these type of applications; despite being well known that they are biodegradable materials (19); they have been proposed in several works to be used as biomaterials. Starch is one of the most abundant and cheap polysaccharides (20,21). An ideal dressing should meet some requirements as absorbing fluids effectively, pleasant in touch and painless in removal, exhibition of high elasticity but also good mechanical strength, good transparency, and can act as a barrier against the microbes.

The present work is aimed at synthesizing PVP/PEG and PVP/PEG/Starch hydrogels for wound dressing by electron beam irradiation of blended PVP, PEG and starch. The physical properties, such as gelation, swelling, water content and degree of water evaporation are examined to evaluate the usefulness of prepared hydrogels for wound dressing. Also, the mechanical properties, crystallinity and microbial test of prepared hydrogels were detected.

2. Experimental

2.1. *Materials*

PVP; average molecular weight of 1,300,000 was purchased by Acros Organics Co. A low molecular weight PEG; 4000 and Starch (corn starch) were supplied by El-Nasr Pharmaceutical Chemicals Co. (Egypt). The tested bacteria included, *Staphylococcus aureus*, *Bacillus subtilis*, and *Escherichia coli* were supplemented by the Regional Center for Mycology and Biotechnology, Al-Azhar University, Cairo, Egypt. The distilled water was used as a solvent.

2.2. *Preparation of PVP/PEG and PVP/PEG/starch hhydrogels*

PVP/PEG and PVP/PEG/Starch hydrogels were prepared by irradiation of an aqueous solution of a polymer sealed in a polyethylene mold. The composition of the homogeneous aqueous solution, which contained 15% wt PVP with 8% wt PEG and 2% wt starch, was chosen to give a gel as close as possible to commercial dressings. This solution was poured into the mold and covered with a thin polyethylene sheet. The mold was subjected to an electron beam with beam current of 25 mA, an acceleration energy of 1.5 MeV, and a power of 37.5 kW generated by the National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority. The prepared crosslinked hydrogels were packaged with boxes and usually exposed with a dose of 25 kGy according to international requirements to ensure sterility of the product.

2.3. *Gel fraction*

To extract the insoluble parts of the hydrogels (i.e., the gelled part), the prepared hydrogels were soaked in water for 48 h at 100°C. Then, they were taken out and washed with hot water to remove the soluble part, dried, and weighed. The gel percent in the hydrogel was determined from Equation 1:

$$\text{Gel } (\%) = (\text{We}/\text{Wg}) \times 100 \quad (1)$$

where We and Wg are dry hydrogel weights after and before extraction, respectively.

2.4. *Water content and swelling*

The gel samples were immersed in distilled water for 48 h at room temperature until the gel reached the equilibrium state of swelling. After the water on the surface of the swollen gels was removed with cellulose paper, the mass was determined. The degree of swelling could be described as water absorptivity of the hydrogels (Equation 2). The swelled gel was then slowly dried to the constant weight and the gel water content was determined as in Equation 3.

$$\text{Swelling} = W_s - W_o/W_o \quad (2)$$

Where, W_s is the weight of the swollen gels and W_o is the weight of the initial gel sample (before being immersed in water).

$$\text{Water content } (\%) = W_s - W_d/W_s \times 100 \quad (3)$$

Where, W_d is the dried gel weight.

2.5. *Degree of water evaporation*

The moisture permeability of the hydrogel wound dressings was determined by measuring the degree of water evaporation across the material as stipulated by a modified ASTM standard method E96 (22). The test involved mounting a disc of the test material in a specially designed cup containing water. The material was positioned across the opening of the cup in an incubator at 37°C and with relative humidity maintained at 80%. The filled cup with the test material in place was hung beneath a balance and its weight determined at hourly intervals to calculate the amount of water loss per hour. By normalizing the value with the exposed surface area of the material, the degree of water evaporation

(%) of the material could be determined gravimetrically by detection of water loss with varying time.

2.6. *Tensile strength and elongation at break*

Dried hydrogel samples were cut into dumbbell shapes (ASTM D 1822-L). Tensile strength and elongation at break were measured with a H1OKS instrument (Hounsfield Test Equipment, Ltd., England) at a crosshead speed of 25 mm/min.

2.7. *Crystallinity determination*

X-Ray Diffraction patterns were obtained with a XD-DI series, Shimadzu apparatus using nickel-filter and Cu-Ka target. This technique was performed to clarify the changes in morphological structure caused during radiation crosslinking process.

2.8. *Scanning electron microscopy*

The lyophilized dried hydrogels were examined with JEOL JSM-5400 scanning electron microscopy (SEM). The surfaces of the polymers were sputter-coated with gold for 3 min.

2.9. *Microbe penetration test*

Antibacterial test was performed by a modified Kirby Bauer technique and a Luria–Bertani (LB) broth method (23). Three bacteria were used as test for microbe penetration for prepared hydrogels in this study. Test bacteria included, *Staphylococcus aureus*, *Bacillus subtilis*, and *Escherichia coli*. The bacteria were cultivated at 37°C in sterilized LB broth (peptone 10 g, yeast extract 5 g, $NaNO_3$ 10 g, distilled water 1000 mL) at 90 rpm in a rotary shaker for 16 h. In the modified Kirby Bauer method, a droplet of 50 mL bacteria medium was dispensed onto an agar plate, then the hydrogel dressings with a thickness of round 3 mm and a size of 7×12 cm^2 were placed and the incubation was continued for 24 h at 37°C. The microbe penetration was observed with day to day for 14 days.

3. Results and discussion

The formation of hydrogels using high-energy radiation can be simply explained as the result of the reciprocal recombination of macroradicals. These, in turn, are generated as a consequence of the direct interaction of the radiation with the polymer or with radicals generated during water radiolysis. If radicals located on different polymer chains are favorably positioned, their recombination results in covalent bonds between polymer chains. If bond-formation processes are faster than are concurrent degradation reactions, then an insoluble gel fraction is formed. Continuous irradiation of such a system increases the amount of the gel, although a part of the macromolecules may still be left unbound (sol) (24). PVP is an example of polymer applied for the synthesis of hydrogel to be used in different biomedical applications (13,25). PVP hydrogels can be obtained by gamma irradiation of PVP/water solutions. The physical and mechanical characteristics of the resultant gel depend on the radiation dose as well as the presence of additive in the solution. The irradiation causes crosslinking between the PVP chain and consequently results in the formation of a polymer network (26). In gel synthesis the presence of chemical substances added to PVP in the starting solution such as PEG and starch as well as the radiation dose influence the mechanical behavior of the resultant product since it influences the network crosslinking density.

3.1. *Gel fraction*

Gel content measurement is an effective method for evaluating the degree of crosslinking of the material. The optimal conditions for PVP hydrogel formation were previously determined (27). The typical hydrogel thus produced presents 85–90% of gel content, (28) as a result of the high efficiency of the formation and recombination of polymeric macroradicals with respect to other competitive reactions. Gel content measurement is an effective method for evaluating the degree of crosslinking of the material. The gel content of PVP/PEG hydrogels with varying its compositions and irradiation dose was shown in Figure 1. It showed that the gel (%) of prepared hydrogels increased with lowered PEG and enhanced irradiation with the range of gel content of 70–94%. This can explained as follows, the PEG does not only act as a plasticizer, but it also reduces the crosslinking reaction and consequently the gelation process due to the PEG chain remains between the PVP chain, avoiding the crosslinking and additionally causing a decrease in the

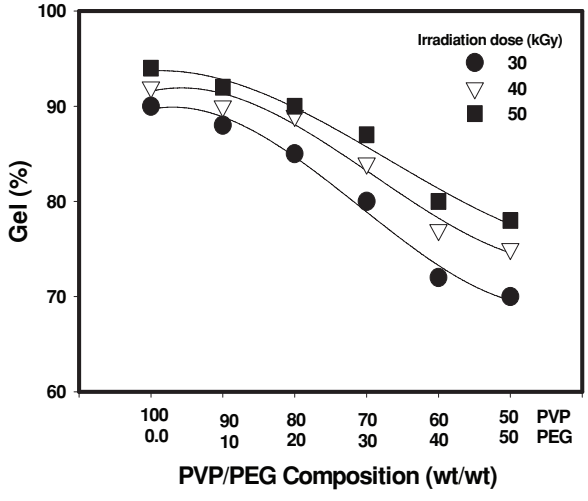


Fig. 1. Effect of PVP/PEG composition on the gel content of PVP/PEG hydrogels at various irradiation doses.

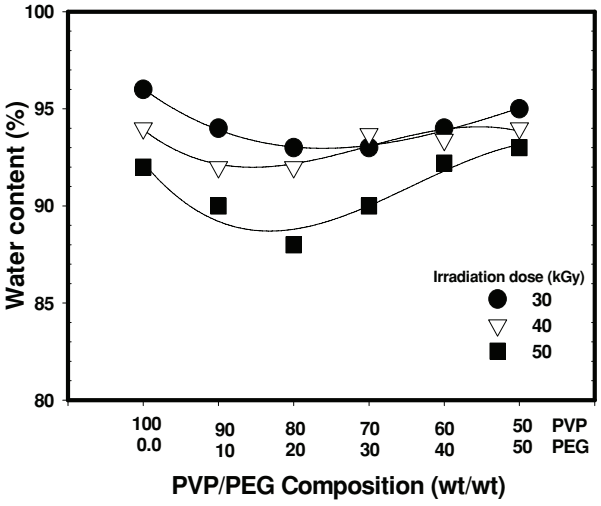


Fig. 2. Effect of PVP/PEG composition on the water content of PVP/PEG hydrogels at various irradiation doses.

physical interactions between PVP chains (26). Also, PEG as an alcohol may act as a radical scavenger, and this effect can be utilized to control (increase or reduce) the gelation% of the prepared hydrogel according to the irradiation dose (5). This effect can reversed with enhancing irradiation dose which cause an additional crosslinking network chains which enhancing gel content.

3.2. *Water content and water absorption*

In the treatment of wounds, the hydrophilic nature of hydrogels is well utilized by helping to maintain a moist environment and promote moist wound healing. Figures 2 and 3 show the effect of PVP/PEG composition and irradiation dose on the water content and swelling of PVP/PEG hydrogels, respectively. It was observed that the water content to be in the range between 88% and 96% and swelling between 12 and 20 g/g with varying PVP/PEG composition and irradiation doses. As shown in Figure 2, it was observed that the water content of PVP/PEG hydrogel tends to increase with increasing PVP concentration, but in turn reduces the degree of swelling, (Figure 3). This fact is certainly understandable because if the initial water content of the same sample increases then the ability of the sample to absorb more water will become lower (29).

3.3. *Degree of water evaporation*

To systematically measure evaporative water loss for the synthesized hydrogels, they were kept at a temperature of 37°C and 80% relative humidity. Evaporative water loss was measured gravimetrically for the hydrogels with various PVP/PEG compositions. The hydrogels were prepared by an irradiation dose of 40 kGy. The evaporative water loss values for the hydrogels are shown in Figure 4. Evaporative water loss continued to rise steadily up to 18 h and then leveled off. No significant differences were observed in the evaporation velocity among the compositions of hydrogels (30). The morphology of the hydrogel surface with evaporative water loss was studied with SEM of the PVP/PEG hydrogel surface which shown in Figure 5, it shows the variation of gel pore shape with its various degrees of water evaporation. The gels have highly porous structure before water loss (Figure 5a), while it degradably collapsed with an enhanced degree of water evaporation. The pore size would be much smaller after water evaporation due to water loss, (Figure 5b) and there is a disappearance of porous structure at full gel drying, (Figure 5c). From a practical point of view, the gel surface facing the wound bed would have open pores. The top surface which gets dried up due to water loss has a collapsed pore structure restricting microbial permeation.

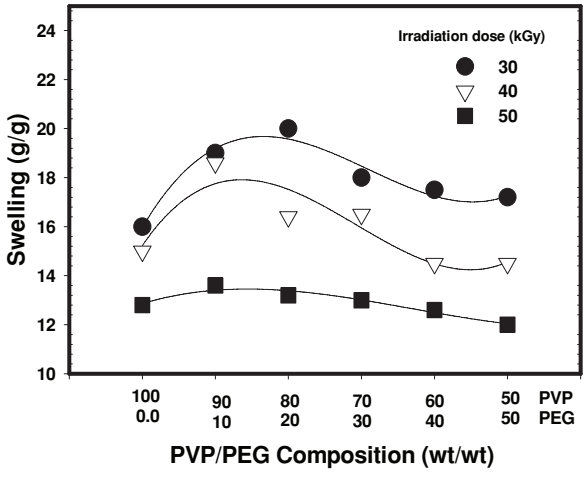


Fig. 3. Effect of PVP/PEG composition on the swelling of PVP/PEG hydrogels at various irradiation doses.

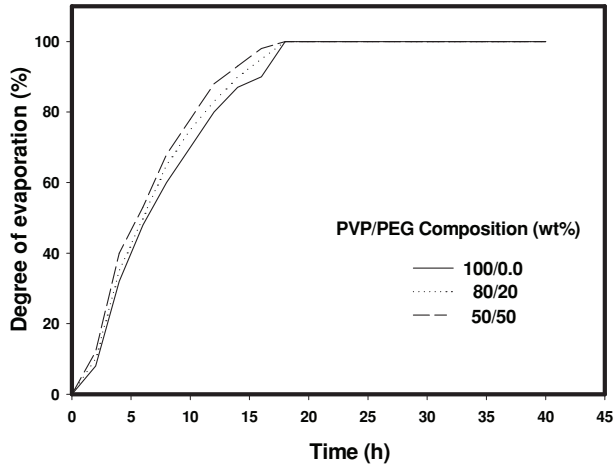
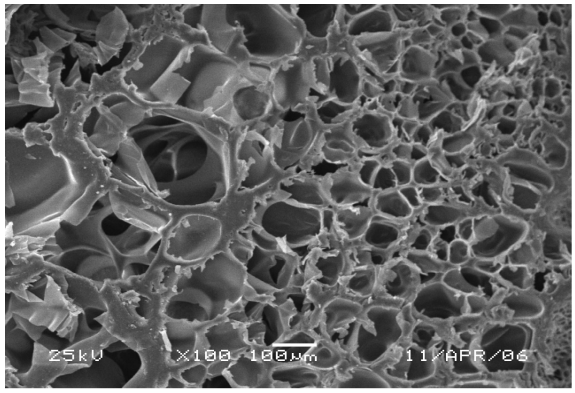
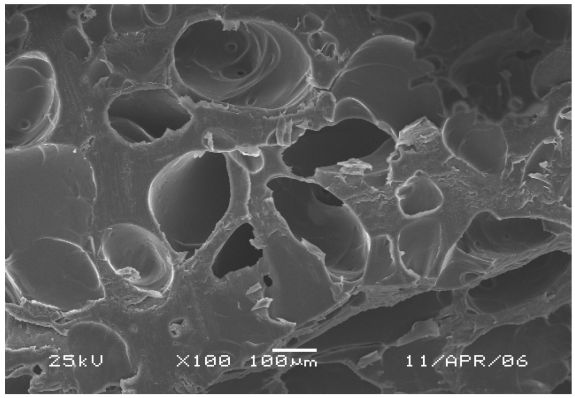


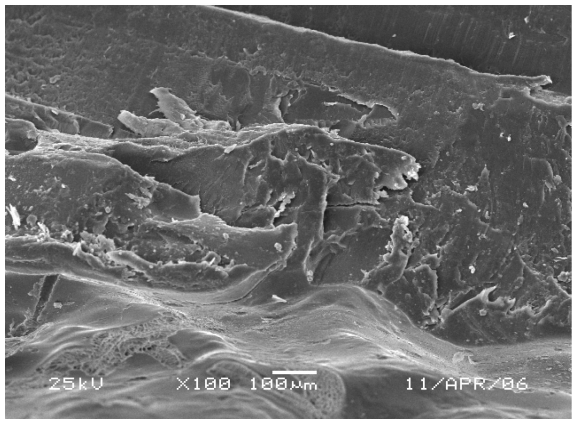
Fig. 4. Degree of evaporation of PVP/PEG hydrogels at different PVP/PEG compositions and various time.



(a)



(b)



(c)

Fig. 5. Morphology and porous structure of PVP/PEG hydrogels with various degrees of water evaporation, (a) 0.0, (b) 50 and (c) 100 (%). PVP/PEG composition, 80/20 wt% and irradiation dose, 40 kGy.

3.4. *Mechanical properties*

One of the major problems in the application of these PVP hydrogels is their relatively poor mechanical strength, attributed to the high degree of hydration of the gel. This work was directed to the study of the mechanical properties of prepared hydrogels to improve it for optimization for wound dressing application. PEG was added to PVP polymers to overcome the low elasticity and flexibility of it. In order to evaluate the mechanical properties of the PVP/PEG hydrogels, the tensile strength of the dry hydrogels was measured, and the results are represented in Figure 6 with respect to their compositions and irradiation dose. The tensile strength increases with increasing of PVP and irradiation dose. The increase of the tensile strength was believed to be due to increased crosslink density (12). Figure 7 showed that the elongation at break increases with increasing PEG content and irradiation dose. This can be explained with higher crosslink density, which reduces the chain mobility and thus reduces the elongation. The presence of PEG normally increase the elasticity of the gel due to the plasticizing effect, that is the PEG chain remains between the PVP chain, avoiding the crosslinking and additionally causing a decrease in the physical interactions between PVP chains.

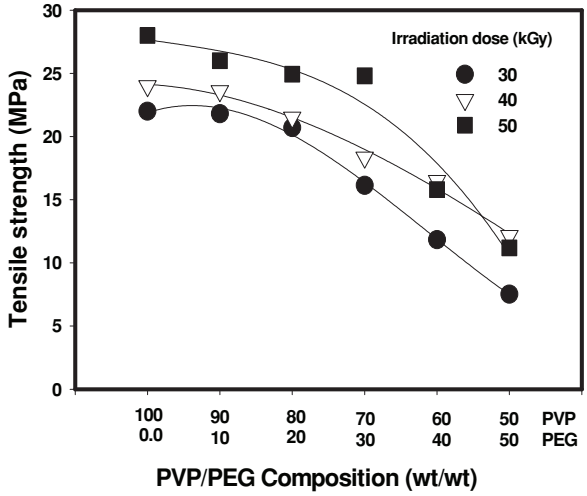


Fig. 6. Effect of PVP/PEG composition on the tensile strength of PVP/PEG hydrogels at various irradiation doses.

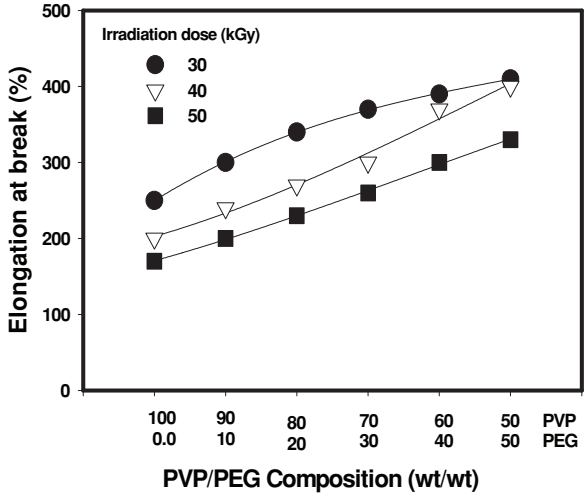


Fig. 7. Effect of PVP/PEG composition on the elongation at break of PVP/PEG hydrogels at various irradiation doses.

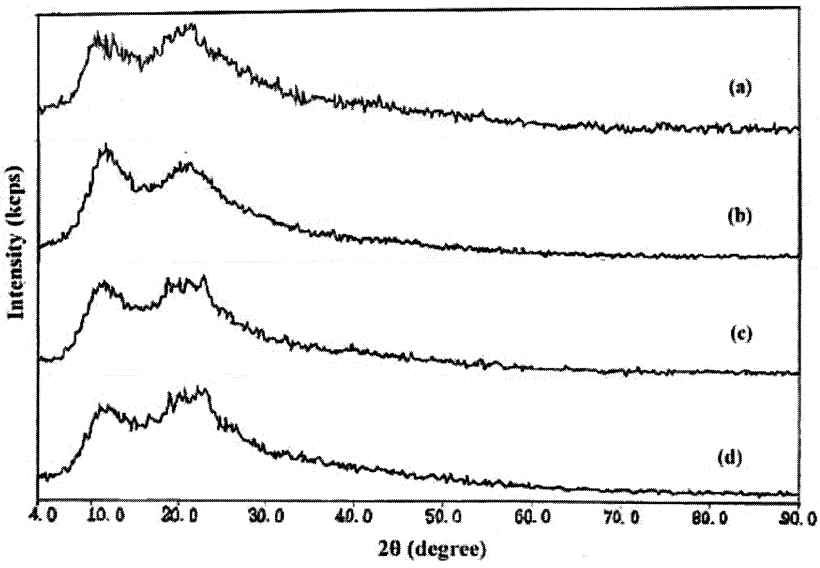


Fig. 8. XRD patterns of PVP/PEG hydrogel wound dressing with various PVP/PEG compositions: (a) 100/0.0, (b) 80/20, (c) 70/30 and (d) 50/50 wt%. Irradiation dose; 40 kGy.

3.5. *Crystallinity*

X-ray diffraction (XRD) studies were performed in order to detect the changes in polymer structure with varying polymer composition at definite irradiation dose; 40 kGy. PVP/PEG hydrogels which prepared at different compositions are examined by using XRD, (Figure 8). It was observed that as the PEG increases the intensity of more intense peaks at $2\theta = 12, 22$ represented the polymer crystal region increases. These results can be attributed to the following; by increasing the PEG content, the crosslinking network structure decreases, so the rearrangement and recrystallization of polymer chains from amorphous state increased.

3.6. *Starch addition*

Although, PVP hydrogels can possess increased properties, and play a significant role in a series of hydrogels as biomedical materials (12), but starch was added to PVP/PEG blend to modify its properties. Various PVP/PEG:Starch compositions were prepared with PVP/PEG composition; 70/30 wt% and irradiation dose; 40 kGy. Table 1 shows the properties PVP/PEG:Starch hydrogels with varying PVP/PEG: starch compositions, it shows that the water content and tensile strength of PVP/PEG: Starch dressing increased with enhancing the added starch, while the swelling and elongation at break were lowered. Nearly, the gel content and degree of evaporation of prepared hydrogels not affected by the added starch. Also, the influence of starch content on the crystallinity of PVP/PEG: Starch hydrogels was detected with XRD, (Figure 9). It showed that with enhanced starch content the intensity of peaks at $2\theta = 12, 22$ represented the polymer crystal region decreased. These results can be attributed to the following; by increasing the starch content, recrystallization and rearrangement of polymer chains restricted by hydrogen bonding resulted between starch –OH groups and C=O in PVP/PEG chains.

3.7. *Microbe penetration test*

The upper surface of the dressings was contaminated with the tested bacteria solution, and then the sample was incubated at 37°C for 24 h. The prepared hydrogel samples

Table 1. Influence of starch content on the properties of PVP/PEG hydrogels. PVP/PEG composition; 70/30 wt% and irradiation dose; 40 kGy

PVP/PEG:Starch Composition (wt%)	*Gel (%)*	*Water content (%)*	*Swelling (g/g)*	*Degree of evaporation (%)*	*Tensile strength (MPa)*	*Elongation at break (%)*
100:0.0	80	80	17	90.0	18	300
90:10	82	83	16	91.0	25	250
80:20	79	86	14	91.5	30	175
70:30	80	89	12	92.0	37	110
60:40	81	92	11	93.0	42	100
50:50	79	94	10	93.5	46	90

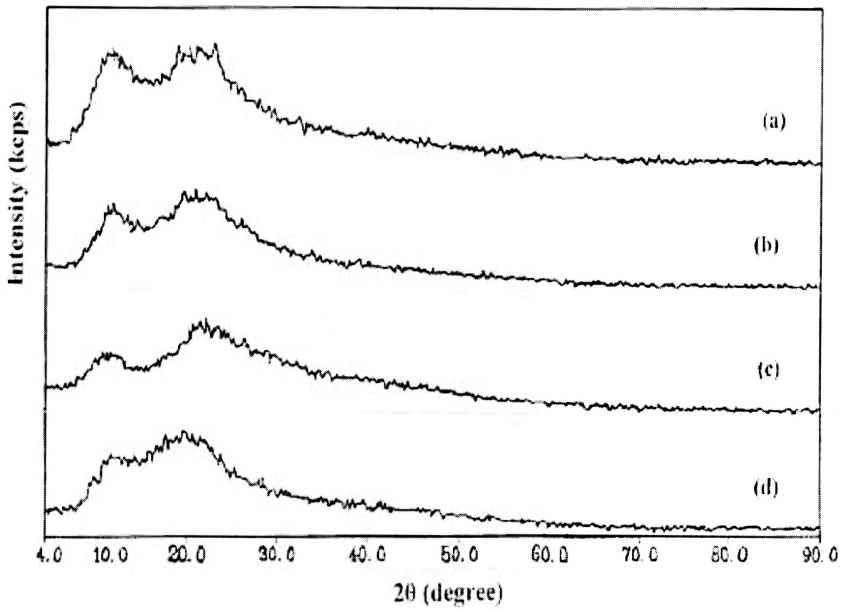


Fig. 9. XRD patterns of PVP/PEG/Starch hydrogel wound dressing with various PVP/PEG:Starch compositions: (a) 100:0.0, (b) 80:20, (c) 70:30 and (d) 50:50 wt%. PVP/PEG composition; 70/30 wt% and irradiation dose; 40 kGy.

were observed daily for 14 days. The test showed that all used bacteria, *Staphylococcus aureus*, *Staphylococcus aureus* and *Escherichia coli* don't pass through all prepared hydrogels. Thus, all prepared hydrogel dressings could be considered as a good barrier against the microbes (31). This characteristic is of importance for the dressings, especially, in protecting the wound from further infection so that it may accelerate the wound healing.

4. Conclusions

Various compositions of both PVP/PEG and PVP/PEG/Starch hydrogels were prepared by electron beam with different irradiation doses. The gel content of prepared dressing increases with increasing PVP content and irradiation dose, and decreased with enhanced PEG contents and not affected by the added starch. Prepared hydrogels have better mechanical properties than that of pure PVP hydrogel, the flexibility was improved with high PEG content while the tensile strength enhanced with higher starch content and irradiation dose. The polymer crystal region increased with enhanced PEG in the feed hydrogel mixture while it decreased with enhanced starch content. The prepared hydrogel dressings could also be considered as a good barrier against microbes. As a result of all these laboratory tests and detection of hydrogel properties, it can be considered that the prepared PVP-based hydrogels with added PEG and starch can meet the requirements of an ideal wound dressing.

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