

SYNTHESIS OF POLYVINYL PYRROLIDONE (PVP)/ κ -CARRAGEENAN HYDROGEL PREPARED BY GAMMA RADIATION PROCESSING AS A FUNCTION OF DOSE AND PVP CONCENTRATION

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ABSTRACT

The aim of this research is to prepare a biomaterial to be used in health care. A series of hydrogels based on polyvinyl pyrrolidone (PVP)/ κ -Carrageenan (KC) has been prepared by radiation technique. PVP (5–15%) were mixed with KC (2%) and irradiated by gamma rays at the doses from 25 kGy to 35 kGy (dose rate 7 kGy/h) at room temperature. The chemical change of hydrogels was characterized using Fourier Transform infra Red (FTIR). Gel fraction, water absorption and water evaporation were determined gravimetrically. Tensile strength and elongation at break was measured using Instron meter. It was found that with the increase irradiation dose and PVP concentration, the gel fraction and tensile strength of hydrogels increase. In contrast the elongation at break and water absorption of hydrogels decrease. The hydrogel of PVP/KC hydrogel produced by gamma radiation can be considered for wound dressings.

Keywords: hydrogel; polyvinyl pyrrolidone; κ -Carrageenan; gamma radiation

ABSTRAK

Penelitian ini bertujuan membuat biomaterial untuk dapat digunakan di bidang kesehatan. Satu seri hidrogel berbasis polyvinyl pirrolidon (PVP)/ κ -karaginan (KC) dipreparasi menggunakan teknik iradiasi. PVP masing-masing dengan konsentrasi 5–15% dicampurkan dengan larutan KC pada konsentrasi 2% dan campuran diiradiasi dengan sinar gamma pada dosis 25 kGy hingga 35 kGy (laju dosis 7 kGy/j) pada suhu kamar. Perubahan kimia hidrogel diukur menggunakan Fourier Transform Infra Red (FTIR). Fraksi gel, air terserap dan air menguap ditentukan secara gravimetri. Perpanjangan putus dan kekuatan tarik diukur menggunakan Instron meter. Hasil penelitian menunjukkan dengan meningkatnya dosis radiasi dan konsentrasi PVP, fraksi gel dan kekuatan tarik hidrogel meningkat. Sebaliknya, perpanjangan putus dan air terserap menurun. Disimpulkan bahwa hidrogel PVP/KC hasil iradiasi gamma dapat dipertimbangkan sebagai pembalut luka.

Kata Kunci: hidrogel; polyvinyl pirrolidon; κ -Karaginan; iradiasi gamma

INTRODUCTION

Hydrogels are cross-linked hydrophilic polymer networks which can absorb large amounts of water without dissolution. Based on their physical properties that similar and compatible with human tissues, hydrogels have been studied extensively for biomedical applications. Particularly, they can be used as soft contact lenses [1-3], tissue engineering scaffolds [4-7], controlled drug-release vehicles [8-11] and wound dressings [12-15]. As wound dressing hydrogels have many advantages. For instance, they can absorb excess of wound exudates, protect the wound from secondary infection and effectively promote the healing process by providing a moisturized wound healing environment [16]. They can also be removed without causing trauma to the wound.

Poly(N-vinylpyrrolidone) (PVP) belongs to the class of water-soluble polymers. From a chemical point of view, PVP is a polymeric lactam with an internal amide bond.

Considering the structure of the monomer unit, PVP has amphiphilic character since it contains a highly polar amide group that confers hydrophilic and polar-attracting properties, and also non-polar methylene groups in the backbone and in the ring that

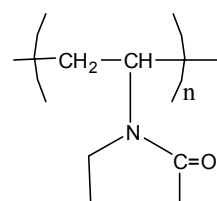


Fig1. Molecular structure of PVP

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confer hydrophobic properties PVP has good biocompatibility and can be used as main component of temporary skin covers and wound dressings. Under exposure to ionizing radiation, PVP undergoes crosslinking to form transparent hydrogels with good biocompatibility [17]. However, for the sake of its inferior fragile mechanical and low swelling capability properties, the application of PVP hydrogels is limited.

Irradiation is recognized as a very suitable tool for the formation of hydrogels. Radiation process has various advantages such as easy process control, possibility of preparing hydrogel and sterilization simultaneously, no necessity to add any initiators and crosslinkers possibly harmful and difficult to remove. They make irradiation as a choice as another methods for the synthesis of hydrogels [18].

κ -Carrageenan, a marine-based polysaccharide, is extracted from red seaweed (*Eucheuma cottonii*), in which it is the major structural component of cell walls [19-20]. *E. cottonii*, typically known as *Kappaphycus alvarezii*, is a spiny, bushy plant consisting of numerous round branches. It is abundant on the inner sides of coral reefs around the Indonesia, Philippines and the island coasts in East Africa [21]. The extract of *E. cottonii* contains almost pure κ -carrageenan, with less than 10% κ -carrageenan. Its high level of κ -carrageenan makes it economically important red seaweed [22]. One of the most important typical characteristics of κ -Carrageenan was its gel solution can change to solid form at room temperature rapidly [23]. In which its can enhance polymerization processing of polymers at radiation processing by solidifying free water and polymers solution. However, if PVP/ κ -Carrageenan blends is irradiated by gamma rays, PVP hydrogels is expected can get obviously increased properties, and play a significant role of hydrogels as biomedical materials.

In this work, PVP/ κ -Carrageenan hydrogels were made by radiation processing for the wound dressing. The physical properties, such as gel fraction, water absorption, water evaporation, elongation at break and tensile strength were examined to evaluate the usefulness of hydrogels for wound dressing.

EXPERIMENTAL SECTION

Materials

Polyvinyl pyrrolidone (Povidone 90 KF) (M_w : 360,000) was supplied from BASF. κ -Carrageenan was purchased from Marcel Carrageenan, Philippine. All the other reagents were of analytical grade and used without further purification. Double distilled water was used for synthesis of hydrogels

Instrumentation

The chemical change of hydrogels was measured using Fourier transform infra red (FTIR) Shimadzu IR-Prestige-21 spectrometer model 800 series, Japan. Tensile strength and elongation at break of hydrogels was determined using Instron meter.

Procedure

Preparation of PVP- κ -Carrageenan hydrogels

κ -Carrageenan powder (2 g) was dissolved in distilled water, stirred at 200 rpm and heated at approximately 80 ± 3 °C for 2 h to form viscous solution. Furthermore, a series PVP solution with concentration ranging from 5 to 15 % (w/v) prepared by autoclaving at 121 °C for 1 h were poured into kappa carrageenan solution and homogenized with stirring at 200 rpm, respectively. The mixture, then poured into double polypropylene (PP) plastic, sealed and irradiated with the doses from 25 kGy up to 35 kGy (dose rate 7 kGy/h) at irradiator *karet* (IRKA) PATIR-BATAN.

FTIR characterization

Fourier–transform infra red spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the κ -Carrageenan and PVP. FTIR spectra were obtained over the range of $400\text{--}4000\text{ cm}^{-1}$ (Shimadzu IR-Prestige-21 spectrometer model 800 series). Samples were milled and mixed with dried KBr powder placed in a sampling cup, 20 scans were required at 2 cm^{-1} resolution with subtraction of the KBr background. FT-IR spectra were also obtained for pure PVP and κ -Carrageenan .for comparison with the hydrogels.

Water absorption

The water absorption of hydrogels was determined by gravimetric method. The gels samples were dried in the oven at temperature of 60 °C up to constant weight. The dried samples were then immersed in distilled water at room temperature. The hydrogels were periodically weighed after the excess surface water was removed with filter paper. The water absorption was calculated as:

$$\text{Water absorption} = (W_1 - W_0) / W_0 \times 100 \% \quad (1)$$

where W_1 is the weight of swollen gel at time t and W_0 is the weight of the dried gels.

Water evaporation

The hydrogels produced by irradiation with dimension of $2 \times 2 \times 0.5\text{ cm}^3$ were placed in petri dish in air at room temperature (33 °C) and 45% humidity. The water evaporation from the hydrogels was measured gravimetrically periodically up to 24 h. Finally,

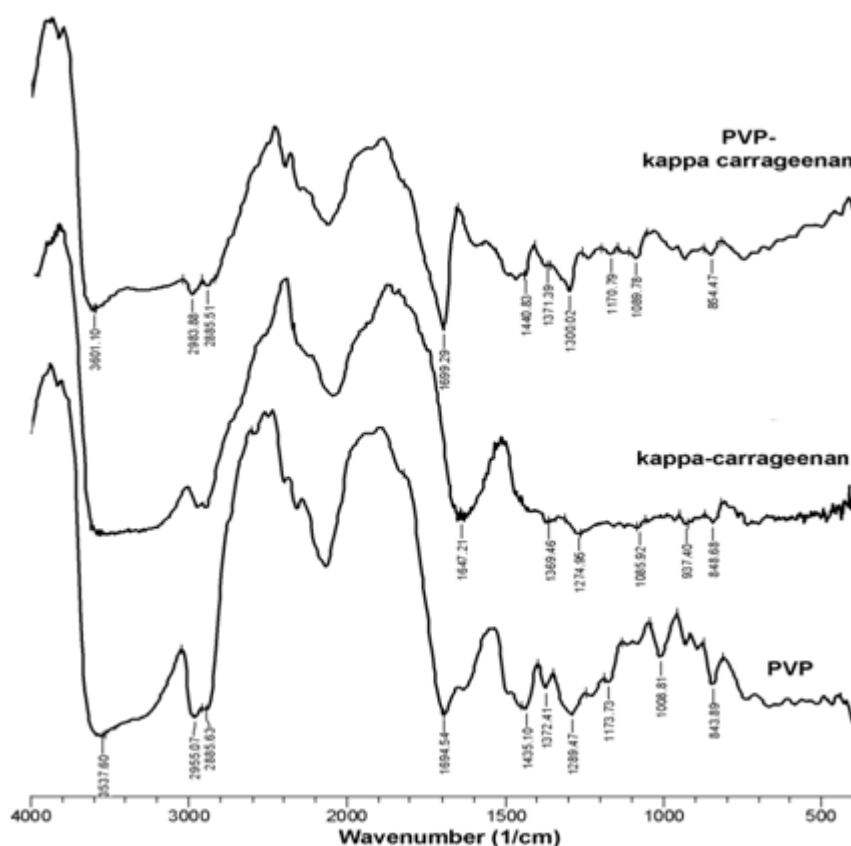


Fig 2. FTIR spectra of PVP, KC, and PVP/KC hydrogel

the water loss percentage was calculated by the following equation:

$$\text{Water lost} = (W_s - W_t) / (W_s - W_d) \times 100\% \quad (2)$$

where W_d is the weight of dried hydrogels, W_s is the initial weight of hydrogels and W_t is the weight of hydrogels after exposed in air at room temperature (33 °C) at time t .

Gel fraction

The hydrogel samples in distilled water were taken into shaker incubator at room temperature to remove soluble fraction for 24 h. The gels were dried to constant weight under vacuum to determine the insoluble fraction in the samples gravimetrically and were calculated as:

$$\text{Gel Fraction} = W_g / W_o \times 100\% \quad (3)$$

where W_g is the weight of dry gel after extraction and W_o is the initial weight of the gel.

Elongation at break and tensile strength

Elongation at break is an important physical parameter of hydrogel representing its elasticity, and measured based on ASTM standard method by using Instron tester instrument. The hydrogels were moulded with dumbbell for the preparation of the standard sizes measurement. Both ends of the pieces were firmly clamped in the jaws of a testing machine. One jaw was

fixed and the other was movable. The movable jaw moved at the rate of 30 mm/min. at room temperature. The resultant data was showed at the recorder. This procedure was repeated for three times for each result. The elongation at break was calculated from the following equation:

$$\text{Elongation at break} = L_1 / L_o \times 100\% \quad (4)$$

where L_o is the original length and L_1 is the final length.

And their tensile strength was calculated from the following equation:

$$\text{Tensile strength} = F/A \quad (5)$$

where F is the amount force of exerted while stretching a sample until the samples fails (kg), and A is the area of the samples (cm^2).

RESULT AND DISCUSSION

FTIR of Hydrogels

FTIR spectra of pure PVP, pure KC and PVP/KC blend are shown in Fig. 2 and spectra are given in the range 400–4000 cm^{-1} . In the spectra of PVP, the peaks observed were at 3460 cm^{-1} for the OH stretching, the peaks at 2927 cm^{-1} and 2880 corresponding to the CH_2 stretching and CH_2 symmetric stretching. The peaks at 1670 cm^{-1} , 1460 cm^{-1} , and 1425 cm^{-1} are assigned to

–C=O stretching, CH₂ bending, and CH₂ bending in α -position of C=O, respectively. The peaks at 1371 cm⁻¹, 1280 cm⁻¹, 1172 cm⁻¹, 1050 cm⁻¹, and 845 cm⁻¹ corresponds to the CH bending, C-N stretching, C-C stretching of the ring and ring of pyrrolidone. FTIR spectra of KC is shown in Fig. 2 with the peaks observed were at 1640–1645 cm⁻¹, 1370–1375 cm⁻¹, 1210–1260 cm⁻¹, 1010–1080 cm⁻¹, 928–933 cm⁻¹, and 840–850 cm⁻¹ are polymer bound water, methylene group, covalent sulfate, glycosidic linkage, 3,6-anhydro-d-galactose and d-galactose-4-sulfate respectively [24]. In the FTIR of PVP/KC hydrogel, the bands that belong to both components can be seen. These results indicate that PVP is miscible with KC. It has been shown that the frequency of the carbonyl stretch is very sensitive to hydrogen bond formation with water molecules. The pyrrolidone rings in PVP contain a proton accepting carbonyl moiety, whereas KC presents hydroxyl as a hydrogen donor. Therefore, hydrogen bonding interactions may take place between these two chemicals moieties in blends of KC and PVP [24]. Abad et al. [24] proposed that irradiation of KC with γ -rays results in radical formation on the carrageenan macromolecule chains and these sites of radical formation become the points of initiation for side chains with PVP.

Gel Fraction

The effect irradiation dose with varying PVP concentration at fixed KC concentration (2%) on the gel fraction of PVP/KC hydrogels are shown in Fig.3. It can be seen with the increase irradiation dose from 15 to 35 kGy with 5% PVP, the gel fraction of hydrogels increase from 40 to 65%. While for 10% PVP, the gel fraction increase from 60 to 78%, and for 15% PVP the hydrogel can reach gel fraction up 90%. Abad et al. [24] conducted a similar study of PVP/KC hydrogel with varying PVP concentration (0–15%) as a function of radiation dose (5–25 kGy) at fixed KC concentration

(6%). They reported that gel fraction rise up beyond the range 25 kGy for 7% PVP, and gel fraction increase with increasing PVP concentration. Optimum gel fraction (~80%) of hydrogel can be reached at a low KC concentration (3%) at a irradiation dose 25 kGy. This is indicated that PVP more reactive to crosslinking while KC is a crosslinking inhibitory. Gamma irradiation of PVP/KC blends would result in the simultaneous crosslinking of PVP, degradation of KC, and grafting of KC to PVP. A combination of these processes may form a PVP/KC hydrogel with a network structure of (a) a semi-interpenetrating polymer network (SIPN) whereby KC is physically entangled within the crosslinked PVP and (b) a grafted network whereby KC is grafted into the PVP backbone. The overall effect of this network could influence the gel fraction.

Water Absorption

Fig. 4 shows the water absorption of different PVP/KC hydrogels as a function of time at varying irradiation dose. The water absorption at initial stage (1–4 h) increase rapidly with time and after some time reaches a limiting value which is the equilibrium value,

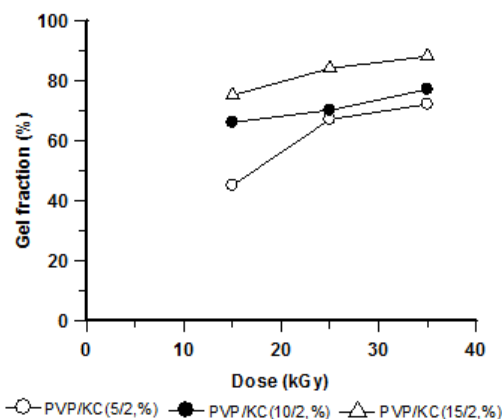


Fig 3. Effect of irradiation dose on gel fraction of PVP/KC hydrogel with varying PVP concentration

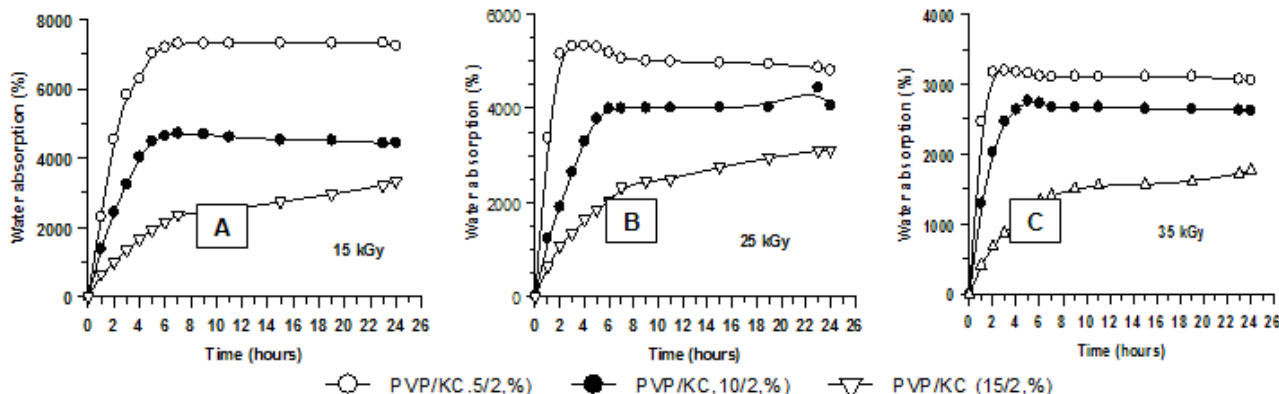


Fig 4. Water absorption of PVP/KC hydrogels with varying PVP concentration prepared with irradiation doses; A) 15 kGy, B) 25 kGy and C) 35 kGy

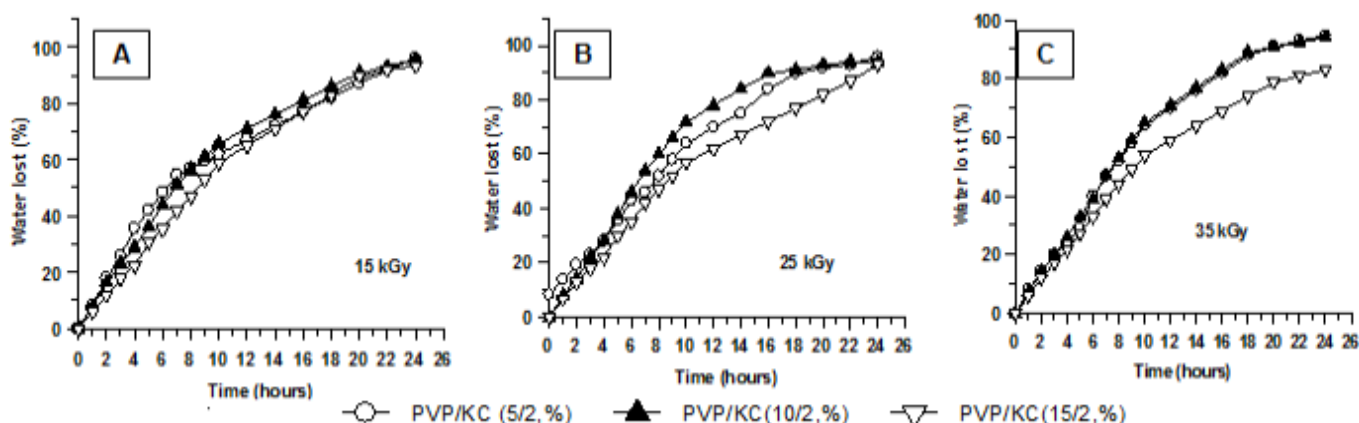


Fig 5. Water evaporation of PVP/KC hydrogels with varying PVP concentration prepared with irradiation doses; A) 15 kGy, B) 25 kGy and C) 35 kGy

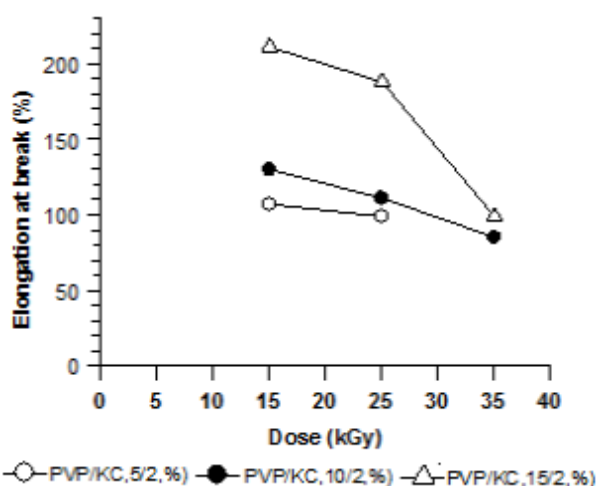


Fig 6. Effect irradiation dose on the elongation at break of PVP/KC hydrogel with varying PVP concentration

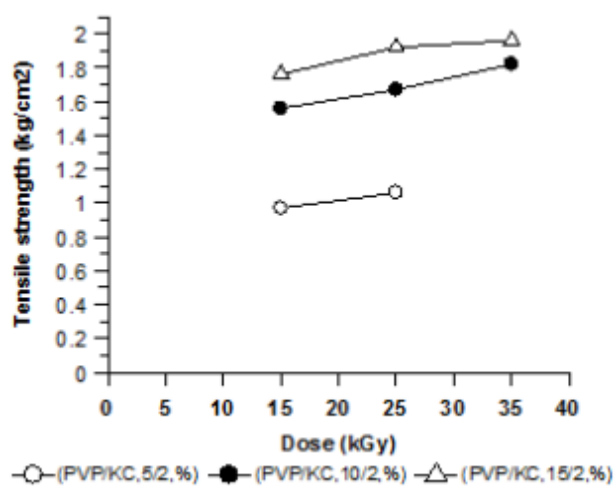


Fig 7. Effect irradiation dose on tensile strength of PVP/KC hydrogel with varying PVP concentration

but decrease with increasing irradiation dose and PVP concentrations. It was found that all hydrogels attained the equilibrium in 8 h with the highest water absorption 7200% of hydrogel PVP/KC (5/2,%) at irradiation dose 15 kGy. This indicates that with increasing irradiation dose, crosslinking of hydrogels increase, and water absorption decreasing.

Water Evaporation

The water evaporation from hydrogels in air at 35 °C and 40% humidity was investigated to examine the possibility of the hydrogels serving as wound dressing. As shown in Fig. 5 the water evaporation from hydrogels prepared by varying irradiation doses and PVP concentration. The water evaporation is very fast in the initial 1 h and then increase gradually up to 24 h for all hydrogels. The hydrogel made from 15% PVP its water evaporation rate tends to decrease with increasing irradiation dose up to 35 kGy. It is known that larger

water absorption can prevent the accumulation of wound exudates, and a smaller evaporation rate can avoid changing the wound dressing too often. Therefore, hydrogels prepared by irradiation dose at 35 kGy for 15% PVP is more suitable as wound dressing.

Elongation at Break and Tensile Strength

The mechanical properties of PVP/KC hydrogels are sensitive to gamma irradiation. However, the tensile strength and elongation at break of PVP/KC samples changed with irradiation dose. Fig. 6 and 7 show the dose-dependent change in elongation at break and tensile strength at room temperature. It was observed that increasing the radiation doses up to 35 kGy reduces the elongation at break and increases the tensile strength of all PVP/KC hydrogel significantly. For 5% PVP at 35 kGy, the elongation at break and tensile strength can not be determined

caused the hydrogel too weak. The elongation at break showed opposite behavior when compared with the tensile strength. However, from the results of Fig.6 and 7, it was found that PVP/KC blend hydrogels had improved elasticity and flexibility, so this kind hydrogel is recommended as wound dressing material.

The variation in elongation at break and tensile strength during irradiation suggests that the efficiency of crosslinking, branching, and degradation, which have opposing effects on these parameters, depends on the composition of the samples and the length of exposure to radiation. The deterioration in the mechanical properties of PVP/KC after irradiation resulted primarily from changes in crosslinking and chain scission.

CONCLUSION

A series of PVP hydrogels with κ -carrageenan were synthesized by irradiation processing. It is found that with increasing PVP content (at a fixed KC concentrations) and irradiation dose, the gel fraction and the tensile strength increase whereas the water absorption capacity, water evaporation and elongation at break decrease.

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