

Synthesis of Starch-Based Plastic Films by Electron Beam Irradiation

H. L. Abd El-Mohdy

National Center for Radiation Research and Technology, P.O. Box No. 29 Nasr City, Cairo, Egypt

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ABSTRACT: Starch-based plastic films were prepared by the electron beam irradiation of starch and poly(vinyl alcohol) (PVA) in a physical gel state at room temperature. The influence of starch/PVA composition, irradiation dose, and plasticizer (glycerol) on the properties of the plastic films was investigated. The gel fraction of the starch/PVA films increased with both the radiation dose and PVA content in the plastic film and decreased with increasing glycerol concentration. The starch/PVA compatibility was determined by measurement of the thermal properties of the starch/PVA blends with various compositions with differential scanning calorimetry. The swelling of the starch/PVA films increased with increasing PVA content and decreasing irradiation dose. Mechanical studies were carried out, and the tensile strength of the films decreased at high starch ratios in the starch-based mixture. This was due to the decrease in the

degree of crosslinking of starch. Furthermore, when PVA, a biodegradable and flexible-chain polymer, was incorporated into the starch-based films, the properties of the films, such as the flexibility (elongation at break), were obviously improved. The tensile strength of the films decreased with increasing glycerol concentration, but elongation at break increased up to a maximum value at a 20% glycerol concentration, and then, it leveled off and decreased slightly. Biodegradation of the starch/PVA plastic films was indicated by weight loss (%) after burial in soil and morphological shape, which was detected by scanning electron microscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 504–513, 2007

Key words: electron beam irradiation; films; mechanical properties; plastics; swelling

INTRODUCTION

Plastics made from petroleum have been used widely throughout the world. With increased applications, the disposal of waste plastics has become a serious problem. Therefore, the development of novel plastics that can be degraded by microorganisms in soil and seawater has recently been emphasized. Since the 1970s, starch has been incorporated into synthesized polymer matrices; in past decades, several efforts have been made to convert starch into a thermoplastic material.^{1–8} The use of starch is increasing in many applications, primarily because starch is a naturally occurring polymer, has a low cost, is easy to handle, and is renewable and biodegradable.⁹ Research has shown that after starch is blended with a synthesized polymer, the synthetic fraction does not have better susceptibility to biodegradation.^{10–12} So the most recent research has focused on pure starch-based materials^{13–16} and starch/degradable polymer blend materials, such as starch/cellulose and starch/poly(vinyl alcohol) (PVA).^{17,18} Starch has been processed in various ways to produce starch plastics. Starch film

preparation by casting from solutions has been reported.⁴ PVA is a versatile polymer with many industrial applications, and it may be the only synthesized polymer whose backbone, mainly composed of C—C bonds, is absolutely biodegradable. PVA samples with number-average molecular weights as high as 100,000 have been reported to be completely degraded by soil bacteria, especially by pseudomonads.¹ The degradability of polymers is a critical function in their application. Currently, no official standard method has been established for the determination of the biodegradability of polymers. The enzyme method,¹⁹ the microbiological method,²⁰ and the soil burial method^{21,22} have been used by different researchers. Biodegradable starch/PVA blend plastics, and Mater-bi (ca. 60% starch, 40% modified PVA, and plasticizers) have been produced on a commercial scale in Japan.²³ However, PVA and starch is a physical blend in Mater-bi. PVA/starch grafted hydrogels can be prepared by irradiation technology.^{24,25} Both PVA and starch are polar polymers; thus, a composite of PVA and starch is likely to produce a material having excellent mechanical properties and barrier behaviors. Because of the chemical reaction between PVA and starch molecules in PVA/starch blend systems induced by irradiation, the tensile strength of PVA hydrogels is obviously improved. According to this result, it is possible to prepare high-property starch-based plastic films by the induction of a chemi-

Correspondence to: H. L. Abd El-Mohdy (hatem_lotfy@yahoo.com).

cal reaction between starch molecules or starch and PVA molecules under the action of ionizing radiation.

Radiation technology has frequently been used to improve the properties of plastic products due to the chemical reaction among polymer molecules under irradiation.²⁶ Starch blended with the synthetic polymer PVA has been studied as a potential biodegradable polymer.¹⁸ Depending on the degree of biodegradability, it seems that PVA might provide a stable support medium for starch films. The mechanical properties and biodegradability of starch/PVA blended films have been reported by several researchers.^{27,28} In this study, starch/PVA film was prepared by casting from solutions as a gel-like mixture of starch, PVA, and water and/or plasticizer. To induce the chemical reaction between starch and PVA molecules and to improve the properties of starch/PVA plastic films, electron beam irradiation (EB) was used to prepare the starch-based plastics by casting from solutions. The effect of preparation parameters, such as starch/PVA composition, irradiation dose, and plasticizer, on the properties of the starch-based plastic films was studied in detail.

EXPERIMENTAL

Materials

Starch (cornstarch) and glycerol were supplied by El-Nasr Pharmaceutical Chemicals Co. (Egypt). Commercial PVA with a molecular weight of about 17,000 was used. In addition, distilled water was used for the preparation of the starch-based plastic films.

Radiation preparation of starch-based plastic films

First, the PVA solution was prepared by the dissolution of PVA in hot water (100°C). After that, the starch/plasticizer (glycerol) premix was mixed with water or the PVA solution and kept at 100°C for 2 h to form a homogeneous, gel-like mixture. The content of plasticizer or PVA was expressed as the mass percentage ratio of plasticizer or PVA to total polymer (starch and PVA), respectively. The total compositions were expressed as the percentage ratio of polymer mass to total mass (polymer, plasticizer, and water). The films were irradiated at room temperature by EB with beam current of 25 mA, an acceleration energy of 1.5 Me V, and a power of 37.5 kW generated by the National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority. Wet starch-based films were dried naturally at room temperature to produce the starch-based plastic films.

Tensile strength and elongation at break

Dried starch-based plastic films were cut into dumb-bell 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.

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. They were taken out, washed with hot water to remove the soluble part, dried, and weighed. The gel percentage in the hydrogel was determined from eq. (1):

$$\text{Gel (\%)} = (W_e/W_g) \times 100 \quad (1)$$

where W_e and W_g are the dry hydrogel weights after and before extraction, respectively.

Swelling measurements

The dried hydrogels of known weights were immersed in distilled water or saline solution at 25°C until the swelling equilibrium was reached (almost 24 h). The gel was removed, blotted quickly with absorbent paper, and then weighed. For accuracy, the experiment was repeated twice for each sample. The following equation was used to determine water uptake:

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

where W_s and W_g represent the weights of the wet and dry gel films, respectively.

Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed with a PerkinElmer model DSC-7. A specimen (≈ 5 mg) of the sample was used for DSC measurements. Indium and zinc standards were used to calibrate the temperature and thermal scale. The measurements were carried out in a N_2 atmosphere from 20 to 230°C at a heating rate of 10°C/min.

Morphology analysis

The surface morphology of the films was examined with a Jeol JSM-5400 scanning electron microscopy (SEM). The surfaces of the polymers were sputter-coated with gold for 3 min.

Soil burial degradation test

Soil burial degradation was performed as described by Thakore et al.²⁹ with a slight modification. Weighed samples were buried in Egyptian sandy clay soil and screened into glass boxes. Soils were kept moist with drinking water and were stored in a room at ambient humidity (48–68%) and temperature (25°C). The thin film samples were buried at a depth of 10 cm. The buried samples were removed after 3 months and were then washed with distilled water and dried at 30°C in a vacuum oven for 24 h. Samples were then allowed to equilibrate to ambient temperature and humidity for at least 24 h before weighing. The weight loss (%) for different buried samples after 3 months of burial in soil was detected as follows:

$$\text{Weight loss (\%)} = (W_b - W_a)/W_b \times 100 \quad (3)$$

where W_b and W_a are the sample weights before and after soil burial, respectively. Weight loss of the specimen was used to indicate degradation in the soil burial test.

RESULTS AND DISCUSSION

Preparation and properties of the starch-based plastic films

Usually, water is regarded as a plasticizer of starch. Here, water was used to prepare gel-like starches with different contents of starch. When the content of starch was less than 10%, a starch solution was formed, and starch-based films were prepared by casting from solutions, and when it more than 10%, compression molding was used to prepare starch-based plastic sheets. When the content of starch was

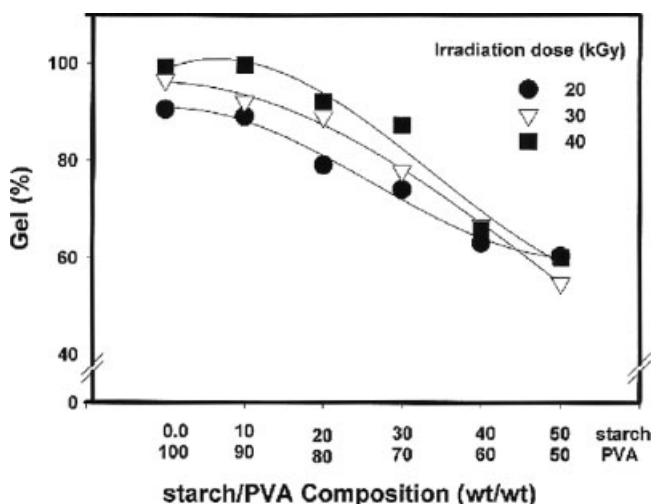


Figure 1 Effect of various starch/PVA compositions on the gel percentage of the starch/PVA plastic films at different irradiation doses (polymer concentration = 7.5% w/v).

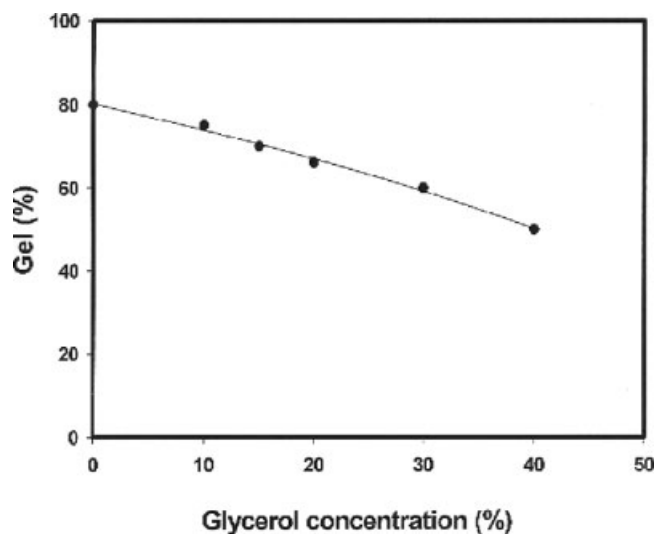


Figure 2 Effect of glycerol concentration on the gel percentage of the starch/PVA plastic films (polymer concentration = 7.5% w/v, starch/PVA composition = 20/80 w/w, and irradiation dose = 20 kGy).

higher than 50%, it was also very difficult to gain homogeneous starch-based sheets by compression molding. In this study, starch-based mixtures containing 0.75–3.75% starch and PVA were prepared and then irradiated by EB at doses of 20, 30, and 40 kGy.

The properties of the prepared starch-based plastic films, such as gel fraction, thermal properties, compatibility, swelling, tensile strength, elongation at break, and degradation in soil, could be influenced by preparation parameters, including starch/PVA composition, irradiation dose, and glycerol concentration.

Gel fraction

Starch-based plastic films were prepared by casting from solutions and irradiated by EB in the physical gel state. To elucidate the formation of starch-based plastic films under irradiation, the gel fraction of starch-based films was determined. Figure 1 shows the effect of various starch/PVA compositions on the gel percentage of the starch/PVA plastic films at different irradiation doses. The gel fraction of the starch/PVA plastic films increased with increasing irradiation dose and PVA content in the plastic film; as a result, there was a crosslinking reaction between the starch and PVA molecules during the irradiation. It manifested that radiation had an important influence on the formation of the starch-based plastic films. Starch in dilute aqueous solution is a kind of radiation degradation polymer,²⁴ but in concentrated solution, it can be crosslinked; this is similar to other natural polymers, such as carboxymethylcellulose.^{30,31} As shown in Figure 2, the gel fraction of the starch-based films decreased with increasing glycerol

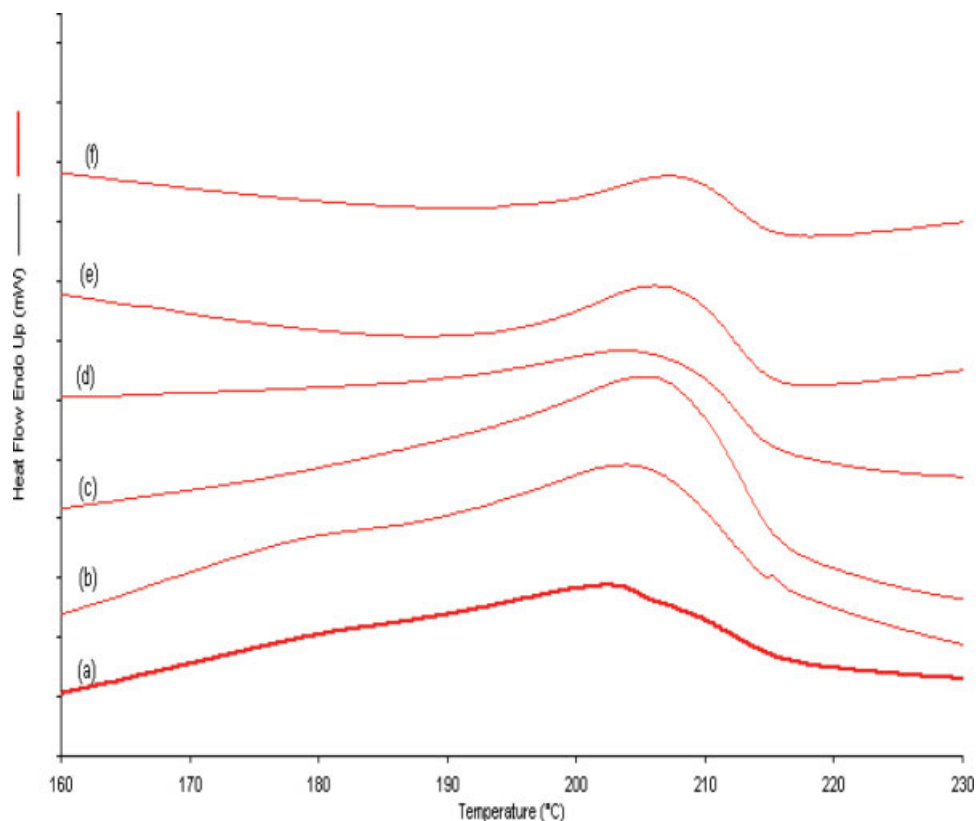


Figure 3 DSC diagram of the different starch/PVA compositions (polymer concentration = 7.5% w/v and irradiation dose = 20 kGy). Starch/PVA compositions: (a) 0 : 100, (b) 10 : 90, (c) 20 : 80, (d) 30 : 70, (e) 40 : 60, and (f) 50 : 50. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

concentration. After glycerol was added to the starch-based films, the gel fraction decreased obviously because glycerol is a kind of chain-transfer mode.²⁵

Thermal properties and starch/PVA compatibility

The incorporation of PVA, a biodegradable and water-soluble crystalline polymer, into starch changes the thermal properties of the material and, thus, modifies the polymer structure at both the molecular and morphological levels. It is widely used because of its flexibility and good film-forming capabilities. The degree of miscibility and the affinity of starch and PVA to form physical intermolecular interactions reflect the extent to which the radiation can affect this blend. Starch/PVA compatibility can be determined by measurement of the change in the thermal properties, melting temperature (T_m), and heat of fusion (ΔH_m) of blend components with DSC. Figure 3 and Table I show the thermal diagram and thermal parameters of the starch/PVA plastic films with different blend compositions, respectively. The DSC endotherms of the starch/PVA blends showed that T_m did not shift much to either lower or higher temperatures with increasing or decreasing portions of starch because it was amorphous and hygroscopic in nature

and did not have a definite T_m , but ΔH_m of PVA changed in the blends. The results obtained reflect the miscibility between the two polymers and suggest interactions between them. The interactions between the blend components (starch and PVA) may have been due to the formation of hydrogen bonds or chemical interactions between the —OH groups of PVA and the —OH groups of starch.

Swelling

The water absorbed by the starch-based plastic films made it very weak and could not be used,³² so the influence of preparation parameters such as starch/

TABLE I
 T_m and ΔH_m Values for Different Starch/PVA Compositions

ΔH_m	T_m (°C)	Starch/PVA composition
16.94	203.16	0 : 100
29.79	205.60	10 : 90
41.12	206.33	20 : 80
22.00	205.33	30 : 70
21.00	206.83	40 : 60
12.12	207.50	50 : 50

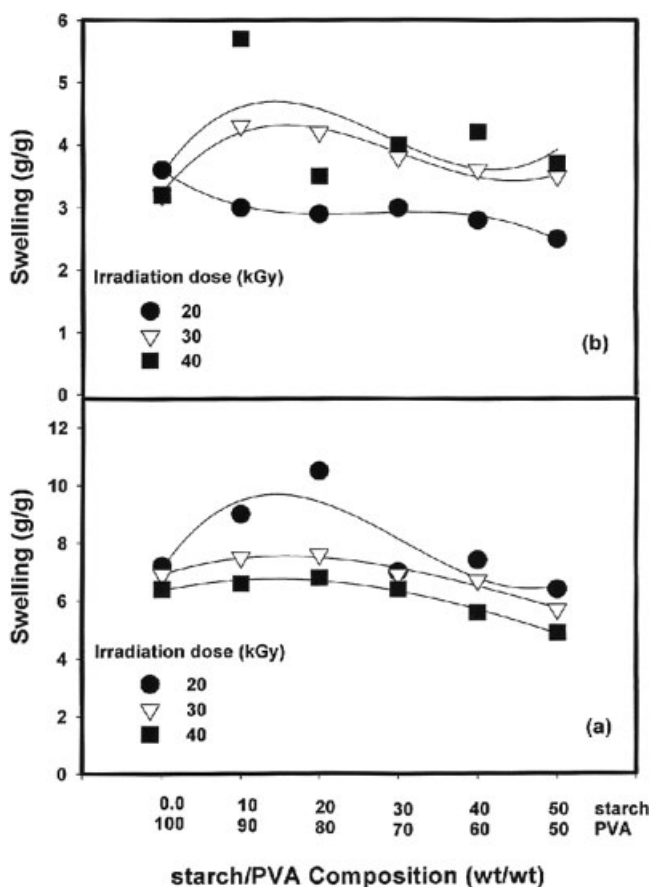


Figure 4 Effect of various starch/PVA compositions on the swelling of the starch/PVA plastic films with different irradiation doses (a) without and (b) with glycerol (polymer concentration = 7.5% w/v, starch/PVA composition = 20/80 w/w, and irradiation dose = 20 kGy).

PVA composition, irradiation dose, and added glycerol on the swelling of the starch-based plastic films was studied. The swelling of the starch/PVA plastic films was concerned with the ratio of the feed polymeric compositions to the irradiation doses. Therefore, the swelling of the starch/PVA films with different compositions without the addition of glycerol was investigated and is shown in Figure 4(a). It was clear that the swelling increased with increasing PVA content and decreasing irradiation dose. PVA constituted the continuous phase in the blend, and the films were very sensitive to water and moisture. However, the use of EB as a crosslinking agent effectively enhanced the films' resistance to disintegration in water and reduced moisture uptake at a high relative humidity, with an improvement in the overall mechanical properties. The swelling of starch/PVA plastic reached a maximum at a copolymer composition of 20 : 80 starch/PVA and 10 kGy. This behavior changed with the addition of glycerol to the starch/PVA polymeric matrix [Fig. 4(b)]. The swelling degree of the starch/PVA plastic films was lower than that in Figure 4(a),

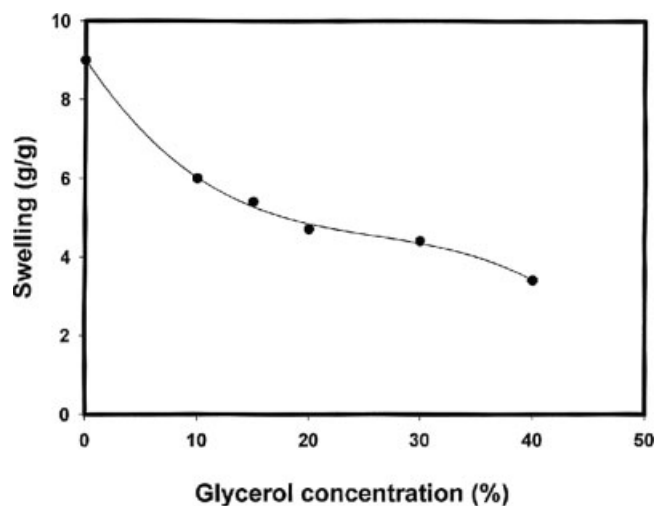


Figure 5 Effect of glycerol concentration on the swelling of the starch/PVA plastic films (polymer concentration = 7.5% w/v, starch/PVA composition = 20/80 w/w, and irradiation dose = 20 kGy).

and it decreased with decreasing irradiation dose. This was confirmed from data shown in Figure 5, which shows that increasing the glycerol concentration in the starch/PVA plastic films led to a reduction in swelling. The results show that the water resistance of the starch/PVA plastic films was improved by increases in the starch content, irradiation dose, and glycerol content.

Tensile strength and elongation at break

The influence of the preparation conditions, such as starch/PVA composition, irradiation dose, and glyc-

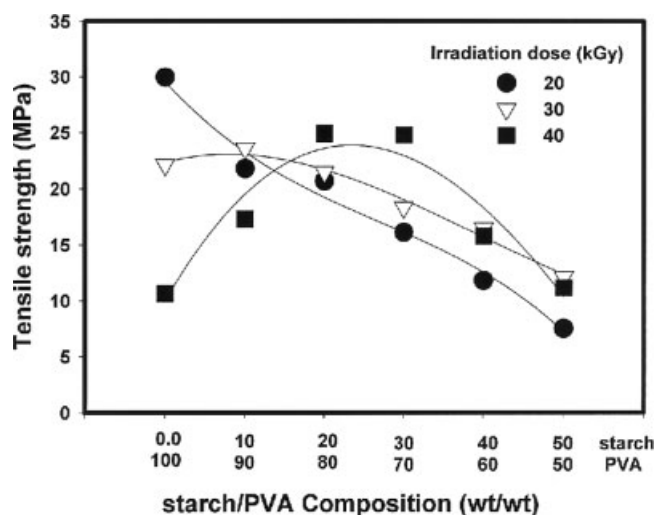


Figure 6 Effect of various starch/PVA compositions on the tensile strength of the starch/PVA plastic films with the addition of glycerol at different irradiation doses (polymer concentration = 7.5% w/v).

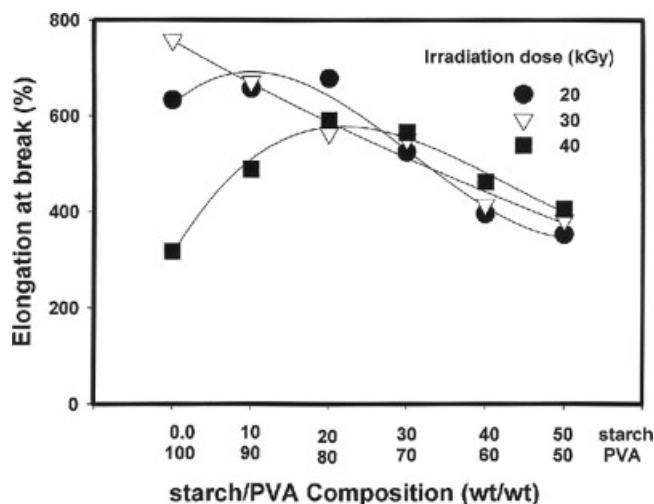


Figure 7 Effect of various starch/PVA compositions on the elongation at break of the starch/PVA plastic films with the addition of glycerol at different irradiation doses.

erol concentration, on the tensile strength and elongation at break of the dry starch-based plastic films was studied. The tensile strength, which is a measure of the resistance to direct pull, is important in machineability and packaging applications. Packaging films composed entirely of starch, however, lack the strength and rigidity to withstand the stresses to which many packaging materials are subjected. The mechanical properties of starch/PVA blends have been reported by several researchers.^{24,25} Figure 6 shows that there were obvious differences in the tensile strength of the starch-based plastic films with increasing irradiation dose and various polymer composition. The tensile strength of the starch-based plastic films increased with increasing irradiation dose and PVA ratio in the

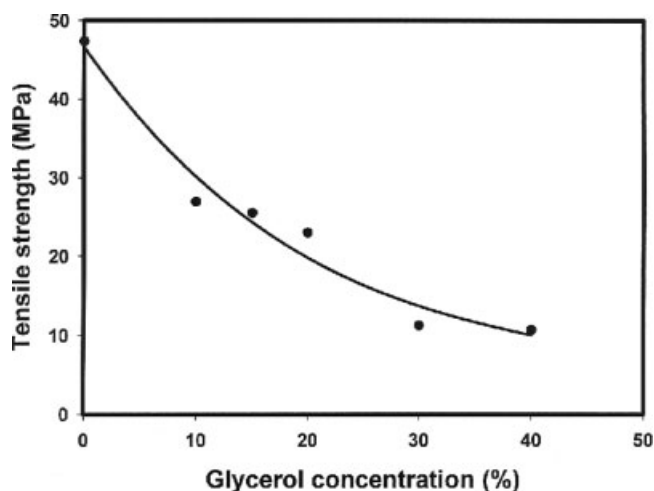


Figure 8 Effect of glycerol concentration on the tensile strength of the starch/PVA plastic films (polymer concentration = 7.5% w/v, starch/PVA composition = 20 : 80 w/w, and irradiation dose = 20 kGy).

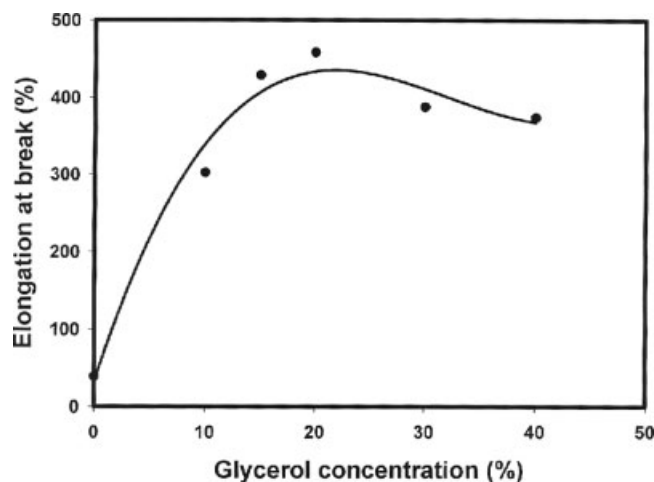


Figure 9 Effect of glycerol concentration on the elongation at break of the starch/PVA plastic films (polymer concentration = 7.5% w/v, starch/PVA composition = 20 : 80 w/w, and irradiation dose = 20 kGy).

polymer blend, but it decreased at high ratios of PVA (starch/PVA = 10 : 90 and 0 : 100) at 40 kGy. The tensile strength increased reasonably with dose due to the chemical crosslinking in the mixture of PVA and starch.

The results indicate that there was a slight variation in the tensile strength for all of the compositions of starch/PVA compared with the tensile strength of the PVA film. The tensile strength of starch-based plastic films was improved by the blending of PVA with starch and radiation modification; this may have been due to the formation of hydrogen bonds or chemical interactions between the —OH groups of PVA and the —OH groups of starch. The tensile strength of

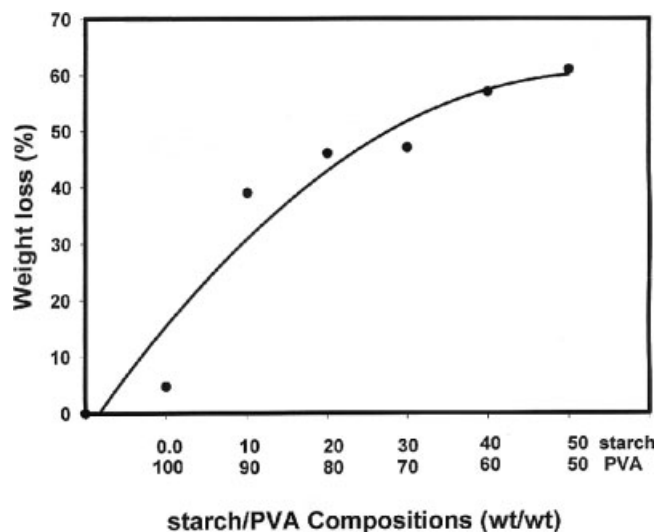


Figure 10 Degradability for the starch/PVA plastic films with different starch/PVA compositions after 3 months of burial in soil (polymer concentration = 7.5% w/v, irradiation dose = 20 kGy, and glycerol concentration = 30%).

plastic films decreased when the content of starch increased, which was attributed to the decrease in the gel fraction of the starch-based films (Fig. 1). With increasing starch content in starch-based mixture, the mobility of the starch molecule obviously decreased. Under irradiation, it was difficult to form chemical networks and interactions between starch molecules. So when starch-based films were irradiated, a lower content of used starch was better than a higher one. Zhai et al.²⁴ found that under the action of ionizing radiation, there was a chemical reaction between PVA and starch molecules in starch/PVA blend systems, and the tensile strength of PVA hydrogels was obviously improved by the incorporation of starch in the

PVA matrix. So PVA was incorporated into starch-based sheets by irradiation to improve the properties of dry starch-based sheets.

The improvement of other properties of the starch-based plastic films, such as the flexibility, was also necessary, so the elongation at break of the prepared starch/PVA films was determined. The influence of the starch/PVA composition and irradiation dose on the elongation at break of the dry starch-based plastic films is shown in Figure 7. Figure 7 shows that the elongation at break increased with increasing PVA and decreasing starch content in the polymer blend, but it decreased with high ratios of PVA (starch/PVA = 10:90 and 0:100) at 20 and 40 kGy. The flexibility of

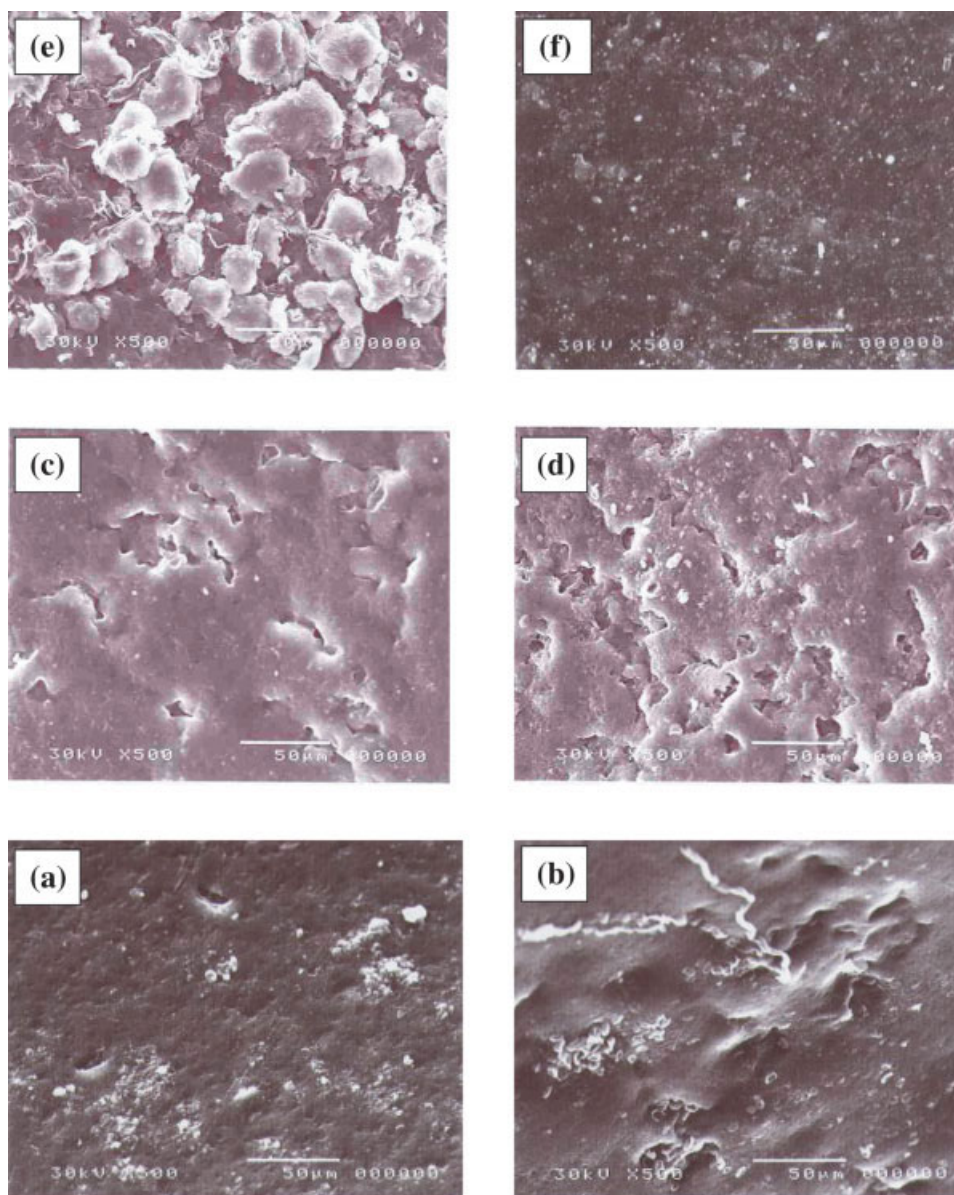


Figure 11 SEM for the starch/PVA plastic films with different starch/PVA compositions after 3 months of burial in soil. Starch/PVA ratio = (a) 0.0 : 100, (b) 20 : 80, (c) 30 : 70, (d) 40 : 60, (e) 50 : 50, and (f) 50 : 50 without soil burial (polymer concentration = 7.5% w/v, irradiation dose = 20 kGy, and glycerol concentration = 30%).

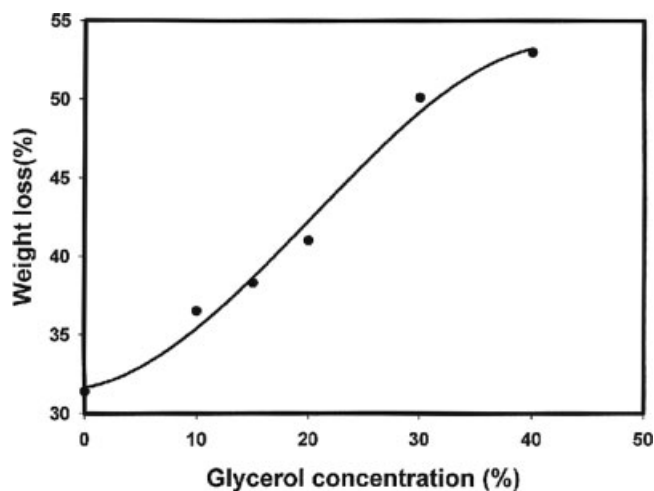
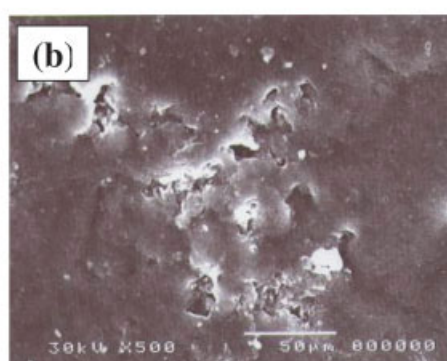
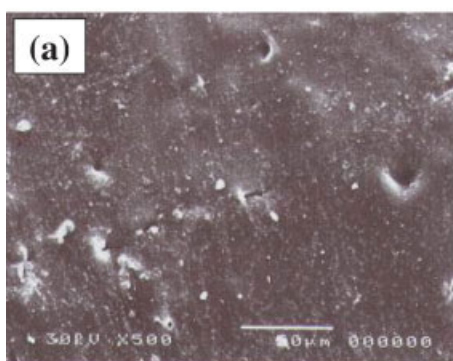
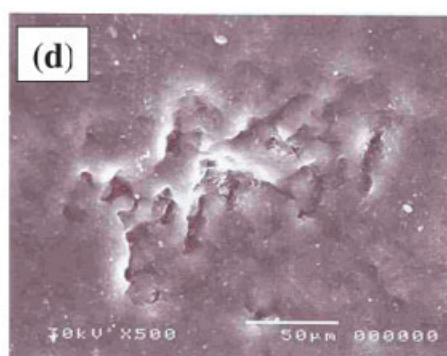
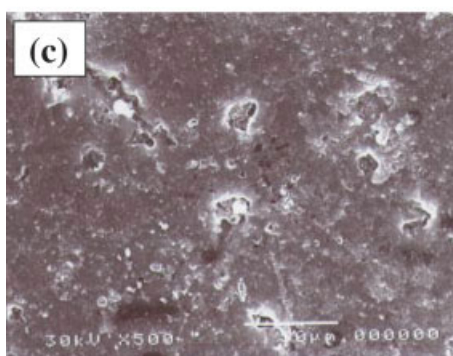
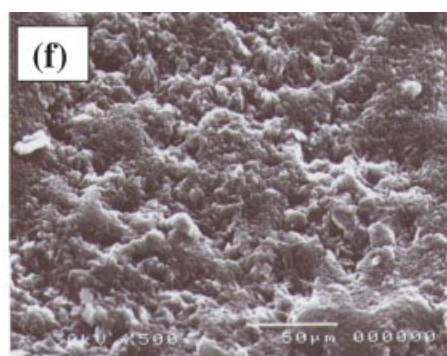
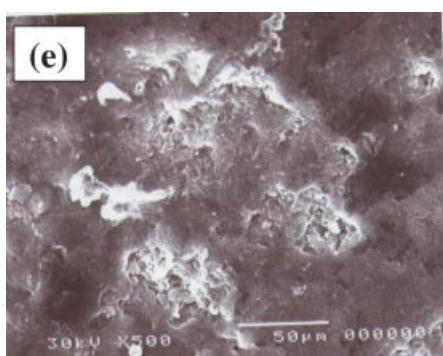


Figure 12 Degradability for the starch/PVA plastic films with various glycerol concentrations after 3 months of burial in soil (polymer concentration = 7.5% w/v and irradiation dose = 20 kGy).

the starch/PVA films improved when PVA was added to the starch.

Because of the amorphous nature of starch, pure starch/PVA films exhibited poor mechanical properties. So, the starch/PVA films were treated with glycerol. The influence of glycerol on the mechanical properties of the dry starch-based plastic films is shown in Figures 8 and 9. At an irradiation dose of 20 kGy, the tensile strength of the dry starch-based plastic films decreased with increasing glycerol concentration (Fig. 8). I explained this behavior by taking into consideration the fact that the increase in the glycerol amount in the blend resulted in a greater mobility of both the starch and the PVA macromolecules. The tensile strength of the blend decreased at a faster rate, especially in the case of a lower concentration of PVA and starch.³³ Also, the elongation at break of the starch/PVA films was influenced by the added glycerol (Fig. 9). The elongation at break increased up to a



maximum value at a 20% glycerol concentration, and then, it leveled off and decreased slightly.

Degradation of the starch/PVA plastic films

To detect starch/PVA biodegradability, the soil burial method was used in this study. The soil burial test is an outdoor experiment and provides a realistic environment where soil humidity, temperature, and type and amount of microorganisms are less controlled and change with season. All of the tested specimens were the same shape and size to avoid the effects of film shape on biodegradability.³³

The biodegradability of the plastic samples was studied by evaluation of their weight loss and was supported by surface morphology with SEM before and after 3 months of burial in soil and with varying starch/PVA compositions and glycerol concentrations. The weight loss percentage of plastic films with different starch/PVA compositions after burial in soil is shown in Figure 10. Figure 10 shows that the weight loss percentage increased with increasing starch ratio in the starch/PVA blends. After 3 months of soil burial, a significant degradation of starch/PVA (composition, 50 : 50) was achieved, as indicated by weight loss (60%). Also, the surface morphology for the starch/PVA plastic films with different starch/PVA compositions showed that the spherical holes appeared when colonization by degrading microorganisms increased with increasing starch content (Fig. 11). The surface morphology of the 50:50 starch/PVA plastic films after and before 3 months soil burial is examined in Figure 11(e,f). Figure 11(e,f) shows that the spherical holes due to colonization by degrading microorganisms appeared in the starch/PVA plastic film buried in soil and did not appear in the other one. Starch blended with a synthetic polymer (PVA) was studied by Ishigaki et al.³⁴ as a potential biodegradable polymer. Depending on the degree of biodegradability, they observed that PVA might provide a stable support medium for starch films. Also, the weight loss percentage of the starch/PVA plastic films increased with increasing glycerol concentration (Fig. 12). It increased significantly up to 53% with 40% glycerol added to the starch/PVA matrix. Also, the surface morphology showed that the spherical holes appeared due to increasing degrading microorganisms with enhanced glycerol content (Fig. 13).

Figure 13 SEM for the starch/PVA plastic films with different glycerol concentrations after 3 months of burial in soil. Glycerol concentration = (a) 0.0, (b) 10, (c) 15, (d) 20, (e) 30, and (f) 40% (polymer concentration = 7.5% w/v, irradiation dose = 20 kGy, and starch/PVA composition = 20 : 80).

It is evident from the results that the degradation of the starch/PVA plastic films in soil increased with increasing starch ratio and glycerol concentration in the starch/PVA films. The pure PVA film exhibited a higher resistance to biodegradation in soil. Tudorachi et al.³³ showed that the weight loss of starch/PVA films was influenced by the blend composition and the plasticizer used. The highest values of weight loss were obtained for samples with a high content of starch. During biodegradation, spherical holes appeared due to colonization by degrading microorganisms. The starch was first consumed by microorganisms, together with the amorphous part of PVA.

CONCLUSIONS

Starch-based plastic films were prepared successfully by EB of cast starch/PVA solutions in a physical gel state. A chemical reaction occurred during irradiation that led to the formation of an intact network structure in the starch-based plastic. The gel fraction of the starch/PVA plastic films increased with increasing irradiation dose and PVA content and decreasing glycerol concentration. The water resistance of the starch/PVA plastic films was improved with increasing starch content, irradiation dose, and glycerol concentration. The tensile strength of starch-based films was improved by the radiation-induced crosslinking reaction in the PVA/starch mixture. The flexibility, or elongation at break, of the starch-based plastic films was improved further by the incorporation of PVA into the starch-based films and the addition of glycerol under the action of ionizing radiation. The degradation of the starch/PVA plastic films in the soil increased with increasing starch ratio and glycerol concentration in the starch/PVA blends. The biodegradability of the starch/PVA plastic films strongly increased with increasing starch and glycerol ratios in the film matrix.

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