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Radiation modification of starch-based plastic sheets

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Abstract

Transparent starch-based plastic sheets were prepared by irradiation of compression-molded starch-based mixture in physical gel state with electron beam (EB) at room temperature. The influence of radiation, plasticizers, water and poly vinyl alcohol (PVA) on the properties of the sheets was investigated. After irradiation, the ductility and tensile strength of the sheets was improved due to the chemical reactions, which was demonstrated by determination of gel fraction and DSC profiles, between starch macromolecules under the action of ionizing radiation. Glycerol, ethylene glycol (EG), poly ethylene glycol (PEG, 600, 1000) was selected as plasticizer to add into starch sheets. The results showed that glycerol was an excellent plasticizer of starch so that the ductility of starch sheets was improved obviously (elongation at break increased). The presence of water was necessary for the preparation of the sheets in this work. With the increasing of the content of starch in starch-based mixture, the tensile strength of the sheets decreased due to the decrease of the degree of the crosslinking of starch. Furthermore, PVA, a biodegradable and flexible-chain polymer, was incorporated into starch-based sheets, the properties of the sheets such as the flexibility (elongation at break) and wet strength was improved obviously.

Keywords: Starch-based plastic sheets; Irradiation; Tensile strength; Physical gel state; Water absorption

1. Introduction

Plastics made from petroleum have been used widespread throughout the world. With increased applications, the disposal of waste plastics has become a serious problem. Therefore, the development of novel plastics that could be degraded by microorganisms in soil and seawater has recently been emphasized. Starch is renewable and biodegradable (Lenz, 1993), since 1970s starch was incorporated into synthesized polymer matrix, in the past decades several efforts have been made to convert starch into a thermoplastic material. (Glenn & Hsu, 1997; Gomes, Ribeiro, Malafaya, Reis, & Cunha, 2001; Kirby, Clark, Parker, & Smith, 1993; Lourdin, Valle, & Colonna, 1995; Ollett, Parker, & Smith, 1991; Otey, Westhoff, & Doane, 1980; Sen & Bhattacharya, 2000; van Soest & Borger, 1997; Spence, Jane, & Pometto, 1995). The research showed that after starch was filled in or blended with synthesized polymer, the synthetic fraction from the oil source has not better susceptibility to biodegradation (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Klemchuk, 1990; Psomiadou, Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1997). So the most recent research has focused on pure starch-based materials (Hulleman, Janssen, & Feil, 1998; Lourdin et al., 1995; van Soest, Benes, & de Wit, 1996; van Soest, & Borger, 1997; van Soest & Kortleve, 1999) and starch/degradable polymer blend materials such as starch/cellulose, starch/poly vinyl alcohol (PVA) (Funke, Bergthaller, & Lindhauer, 1998; Ishigaki, Kawagoshi, Ike, & Fujita, 1999).

Usually native starch contains about 30% amylose, 70% amylopectin and less than 1% lipids and proteins from plant. Physical gels and dispersions from native, purified amylose or amylopectin starches showed differences in properties such as phase separation, physical gelation, aggregation and crystallization (Hulleman et al., 1999; Jane & Chen, 1992; van Soest & Borger, 1997; Yuryev, Nemirovskaya, & Maslova, 1995). Starch has been processed in various ways to produce starch plastics. Starch film prepared by casting from solutions has been reported (Lourdin et al., 1995). But due to high cost of preparation from solution, most

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investigations related to starch products were concentrated on the thermomechanical processing techniques such as compression molding, extrusion molding and injection molding of wet starch (the ratio of water to starch was 10–40%). During the thermomechanical processing, a complex of starch network was formed in starch products attributed to amylose and amylopectin unit interactions and entanglements as well as various crystal structures (Glenn & Hsu, 1997; Gomes et al., 2001; Hulleman et al., 1999; Kirby et al., 1993; Ollett et al., 1991; Otey et al., 1980; Sen & Bhattacharya, 2000; van Soest & Borger, 1997; van Soest & Kortleve, 1999; Spence et al., 1995). The influence of starch sources, starch components, starch molecular mass and plasticizer, such as water and polyols, has been studied to improve the mechanical properties of starch plastics. However, poor mechanical properties constituted one of the major unresolved problems. Although their tensile strength may be rather high (30–60 MPa), these materials are fragile with low elongation at break and poor water resistance. After absorbing water, they were very weak and could not be used. (Glenn & Hsu, 1997; Hulleman et al., 1998; Kirby et al., 1993; Lourdin et al., 1995; Ollett et al., 1991; van Soest et al., 1996).

PVA is a versatile polymer with many industrial applications, and it may be the only synthesized polymer, whose backbone mainly composed of c–c bond, that 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 (Lenz, 1993). Biodegradable starch/PVA blend plastics, 'Mater-bi' (about 60% starch, 40% modified PVA and plasticizers), have been produced in commercial scale in Japan (Iwanami & Uemura, 1993). But PVA and starch is physical blend in Mater-bi. In our previous work PVA/starch grafted hydrogels have been prepared by irradiation technology (Zhai, Yoshii, Kume, & Hashim, 2002). Due to the chemical reaction between PVA and starch molecules in PVA/starch blend systems induced by irradiation, the tensile strength of PVA hydrogels was improved obviously. According to this result, we consider it is possible to prepare high-properties starch-based plastic sheets by inducing chemical reaction between starch molecules or starch and PVA molecules under the action of ionizing radiation. Radiation technology has been used frequently to improve the properties of plastic products due to the chemical reaction among polymer molecules under irradiation (Bhattacharya, 2000; Gehring, 2000). In this work starch-based plastic sheets were prepared by compression-molding of gel-like mixture of starch, plasticizer, water and/or PVA. In order to induce the chemical reaction between starch molecules or starch and PVA molecules to improve the properties of starch-based plastics, starch-based sheets prepared by compression-molding was irradiated by EB. The effect of radiation on formation and properties of starch-based plastic sheets was studied in detail.

2. Experimental

2.1. Materials

Starch (cornstarch), was supplied by Gunei Chemical Industrial Co. LTD, Japan. PVA-117 was supplied by Kuraray Co. LTD, Japan. Glycerol, ethylene glycol (EG), poly (ethylene glycol) (PEG, 600, 1000) and dimethyl sulfoxide (DMSO) were obtained from Kanto Chemical Co. Inc. Japan. In addition, Distilled water was used for the preparation of gel-like starch.

2.2. Irradiation preparation of starch-based plastic sheets

At first, PVA solution was prepared by dissolving PVA in hot water (100 °C). After that, starch/plasticizer(glycerol, EG or PEG) premix was mixed with water or PVA solution and kept at 100 °C for 2 h to form homogeneously gel-like mixture. The content of plasticizer or PVA was expressed as mass percent ratio of plasticizer or PVA to total polymer (starch and PVA), respectively. The total compositions were expressed as percent ratio of polymer mass to total mass (polymer, plasticizer and water). The gel-like mixture in hot state was pressed by cold-presser to make starch-based sheets (thickness of wet sheet: 0.5 mm). The sheets were irradiated at room temperature by EB, with beam current of 1 mA and acceleration energy of 2 MeV, generated by the Cockroft Walton EB Accelerator. After that, wet starch-based sheets were dried naturally at room temperature to gain starch-based plastic sheets.

2.3. Tensile strength and elongation at break

Dried starch-based plastic sheets were cut into dumbbell shape (ASTM D-1822-L). Tensile strength and elongation at break were measured using strograph-R1 Material Tester (Toyoseiki Co. Ltd, Japan.) with a crosshead speed of 50 mm/min.

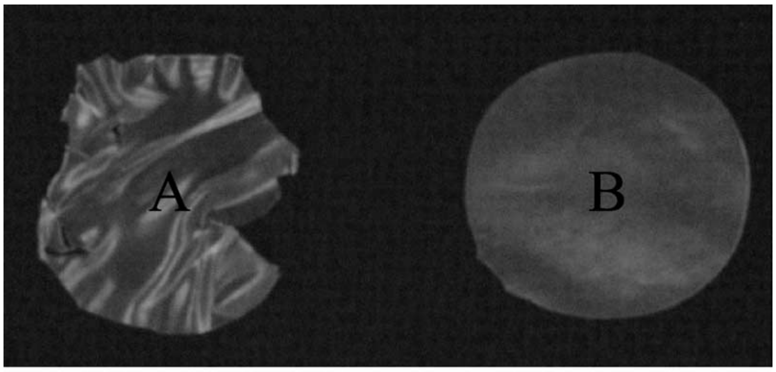
Tensile strength and elongation at break of wet starch/PVA blend sheets (after dry starch/PVA blend sheets absorbing water to the equilibrium, 24 h) were also determined by using the above methods.

2.4. Gel fraction

Starch-based sheets were put into stainless net of 200 mesh and immersed in DMSO for 72 h at room temperature to extract the sol part. After that, the samples were washed thoroughly by distilled water and dried to constant weight at 50 °C. Gel fraction was calculated as

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

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



A: without irradiation; B: with irradiation (30kGy)

Fig. 1. The photographs of starch-based plastic sheets after drying naturally at room temperature.

2.5. Thermal analyses

DSC measurements were performed with a Perkin–Elmer Model DSC-7. The evaporation endotherm of water from wet starch-based sheet was determined from 20 to 200 °C at a heating rate of 10 °C/min under nitrogen.

2.6. Water absorption of starch-based plastic sheets

Dried starch-based plastic sheets were immersed in distilled water at room temperature to the equilibrium (24 h). After that the sheets were dried to the constant weight at 50 °C. The content of water adsorbed (CWA) in starch-based sheet was calculated as:

$$\mathrm{CWA} = W_e - W_d/W_d \quad (2)$$

Where W_e is the weight of starch-based sheet at the adsorbing equilibrium and W_d is the dry weight of starch-based sheet.

3. Results and discussion

3.1. Radiation formation of starch-based plastic sheets

Starch-based plastic sheets were prepared by compression-molding in physical gel state, and then a part of wet starch-based sheets were irradiated by EB. Wet starch-based sheets with or without irradiation were dried naturally at room temperature. Fig. 1 showed that there was obvious difference between the sheets with and without irradiation. The sheets without irradiation shrunk and broke into the fragment after drying naturally at room temperature (Fig. 1A). But after starch-based sheet in physical gel state was irradiated, an intact, smooth starch-based sheet was formed after drying at the same condition (Fig. 1B). It manifested that radiation had an important influence on the formation of starch-based plastic sheets.

3.1.1. The influence of dose and plasticizers on properties of starch-based plastic sheets

The influence of dose and plasticizers on properties of dry starch-based plastic sheets was shown in Fig. 2. In the dose range of 30–70 kGy, the tensile strength of dry starch-based plastic sheets increased with the increasing of dose. When the dose increased further, the tensile strength leveled off or decreased slightly. After adding glycerol into starch sheets, the tensile strength decreased obviously, but dry starch-based sheets began to display the plasticity and flexibility when the glycerol content was higher than 20%. The change of elongation at break with glycerol content was showed in Fig. 3. When the amount of glycerol was 30% in starch-based sheet, elongation at break reached 50%. However, no obvious change of elongation at break was observed with the changing of dose.

EG and PEG were also excellent plasticizers to plastics. In this work, EG, PEG600 and PEG1000 were used to plasticize starch. The results showed that dry starch-based sheets containing PEG, with or without irradiation, broke into the small fragment after dried at

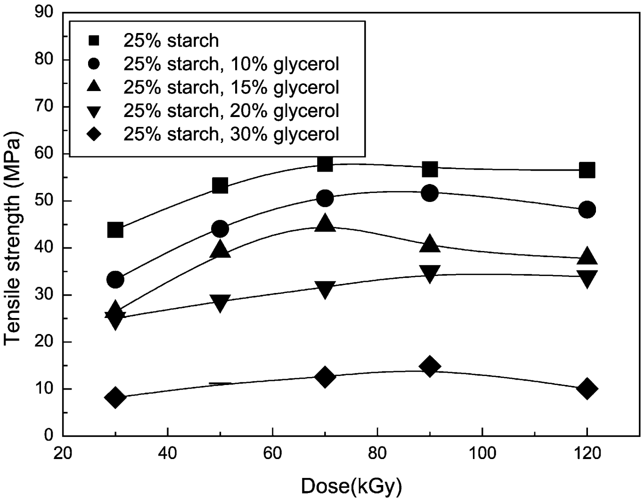


Fig. 2. The tensile strength of starch-based plastic sheets after drying naturally at room temperature.

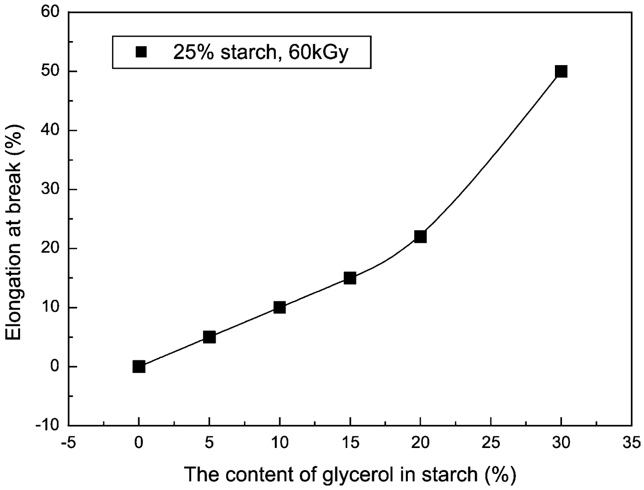


Fig. 3. Elongation at break of starch-based plastic sheets after drying naturally at room temperature.

room temperature. Irradiated starch-based sheets containing EG could form intact sheets after dried at room temperature, but their tensile strength and ductility was worse than that of dry starch-based sheet containing glycerol (Fig. 4).

3.1.2. Discussion on the formation mechanism of starch-based plastic sheets

In the above experiment, why was there an obvious different result between the starch-based sheets before and after irradiation? In order to elucidate the formation mechanism of starch-based plastic sheets under irradiation, the gel fraction of starch-based sheet was determined (Fig. 5). From Fig. 5 it could be found that there was crosslinking reaction between starch molecules during the period of irradiation. Starch in dilute aqueous solution is a kind of radiation degradation polymer (Zhai et al., 2002). But in concentrated solution it can be crosslinked, which is similar to other natural polymers such as carboxy methylcellulose (CMC), etc. (Fei, Wach, Mitomo, Yoshii, & Kume, 2000; Liu, Zhai, Li, & Wu, 2002). After adding glycerol into starch-based sheets, the gel fraction decreased obviously because glycerol was also a kind of chain transfer agent. It was not difficult to explain that the improvement of tensile strength (Fig. 2) of starch-based plastic sheets attribute mainly to the crosslinking reaction of starch molecules.

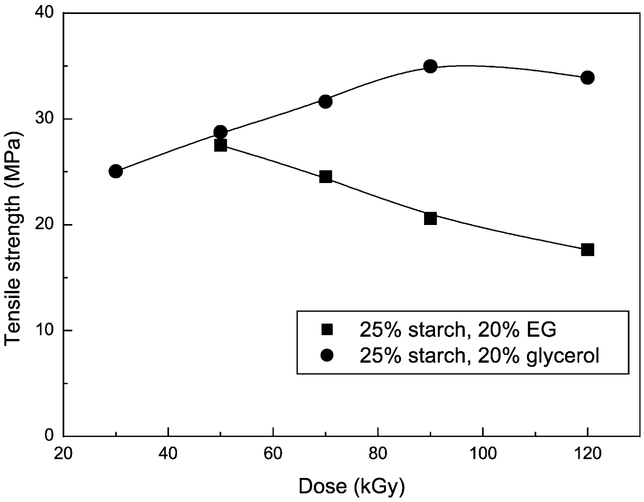


Fig. 4. Effect of plasticizer on the tensile strength of dry starch-based sheets.

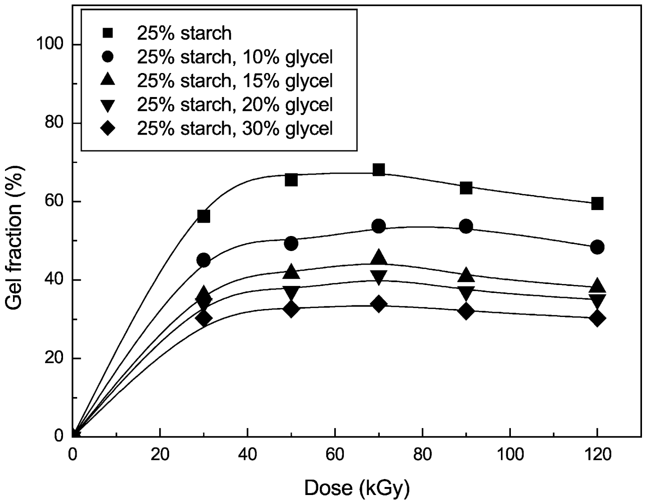


Fig. 5. Gel fraction of starch-based plastic sheets.

It was reported that at high water content, starch in physical gel state existed as two-phase systems due to the thermodynamic immiscibility of two main components (linear amylose and branched amylopectin) of starch (Yuryev et al., 1995), which meant that in physical gel state there were different interactions between amylose-water and amylopectin-water. So when water evaporated from starch-based sheets with high water content, evaporation enthalpy of water from amylose was different with that from amylopectin. In this work, evaporation endotherm of water from wet starch-based sheets without irradiation was shown in Fig. 6 (solid line). There were obvious two

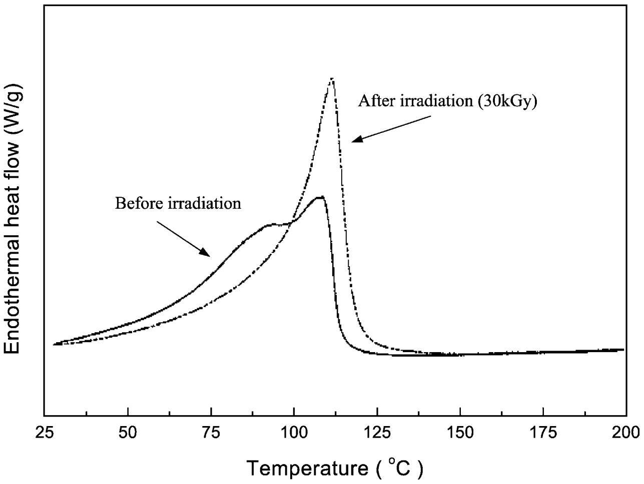


Fig. 6. DSC evaporation endotherm of water from starch-based sheets before drying.

peaks: One with a peak temperature of 91.0 °C, and the other one with a peak temperature of 106.5 °C. At the gelatinization endotherms of starch, two peaks were also observed due to the different melting of amylose and amylopectin crystallinity during gelatinization (van Soest & Borger, 1997). However, after irradiation there was only one peak in evaporation endotherm of water from wet starch-based sheets (dash and dot line). It suggested that under the action of ionizing radiation an intact complex starch network was formed as a result of amylose and amylopectin chain–chain chemical interactions and physical entanglements. Before irradiation, because there are different interactions between amylose-water and amylopectin-water, starch-based sheets shrunk and broke into the fragment when it was dried. But after starch-based sheet in physical gel state was irradiated, an intact complex starch network was formed. There were nearly same interactions between water and different macromolecules (amylose and amylopectin) in network. So an intact starch-based sheet could form after drying at the same condition.

In the above work, an excellent dry starch-based plastic sheet was gained by irradiation of compression-molding starch-based sheet in physical gel state. In order to further elucidate the influence of irradiation on the formation of starch-based plastic sheets, it was tried to prepare sheets from irradiated gel-like starch by compression-molding. However, homogeneous sheets could not be gained due to the crossliking reaction between starch molecules during irradiation, after irradiation it was difficult to form homogeneous sheets. It manifested further that intact network structure in starch-based plastic sheets was formed and fixed on the spot during the period of irradiation.

3.1.3. The influence of the content of starch in physical gel state on properties of starch-based plastic sheets

Usually water was regarded as a plastisizer of starch. Here water was used to prepare gel-like starch with different content of starch. When the content of starch is less than 10%, a starch solution was formed and starch-based sheets could not be prepared by compression-molding. When the content of starch was higher than 50%, it was also very difficult to gain homogeneous starch-based sheets by compression-molding. In this work, starch-based mixture containing 15–50% starch was prepared, and then was irradiated at 30 kGy. The results (Fig. 7, curve A) showed that the tensile strength of dry starch-based plastic sheets decreased when the content of starch increased from 15 to 50%, which attributed to the decrease of gel fraction of starch-based sheets (Fig. 7, curve B). With increasing of the content of starch in starch-based mixture, the mobility of starch molecule decreased obviously. Under irradiation it was difficult to form chemical network and interaction between starch molecules. So when starch-based sheets were irradiated by EB, lower content of starch was better than higher one.

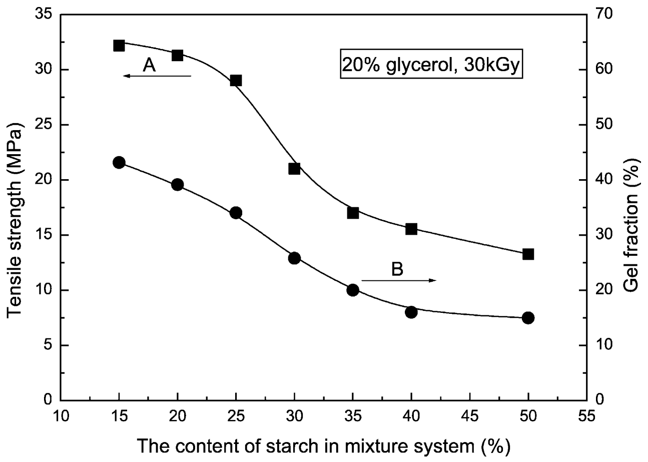


Fig. 7. The change of tensile strength and gel fraction of dry starch-based sheets with the content of starch in mixture.

3.2. Influence of PVA on the properties of starch-based plastic sheets

In the above experiment, the tensile strength of dry starch-based plastic sheets was improved by radiation modification, but the improvement of other properties of dry starch-based sheets such as the flexibility and water resistance is also necessary. Water sensitivity was an important criterion for many practical applications of starch plastics. Pure starch-based plastics had poor water resistance. After adsorbing water, the tensile strength decreased dramatically (Kirby et al., 1993; Ollett et al., 1991; van Soest et al., 1996). The improvement of flexibility and water resistance will be studied further in followed work.

PVA, a biodegradable and flexible-chain polymer, has been incorporated into starch plastics by physical blending to modify the properties of starch plastics (Iwanami & Uemura, 1993). In our previous work it has been found that under the action of ionizing radiation, there was chemical reaction between PVA and starch molecules in PVA/starch blend systems and the tensile strength of PVA hydrogels was improved obviously by incorporation of starch (Zhai et al., 2002). So PVA will be incorporated into starch-based sheets by irradiation to improve the properties of dry starch-based sheets.

The influence of PVA on tensile strength and elongation at break of dry starch/PVA blend plastic sheets was shown in Fig. 8. After incorporating PVA into starch-based sheets, with increasing of the content of PVA, tensile strength of dry starch/PVA blend plastic sheets decreased, but the elongation at break increased obviously, i.e. the flexibility of starch-based sheets was improved after blending with flexible-chain PVA. The experiment also showed that at certain composition of

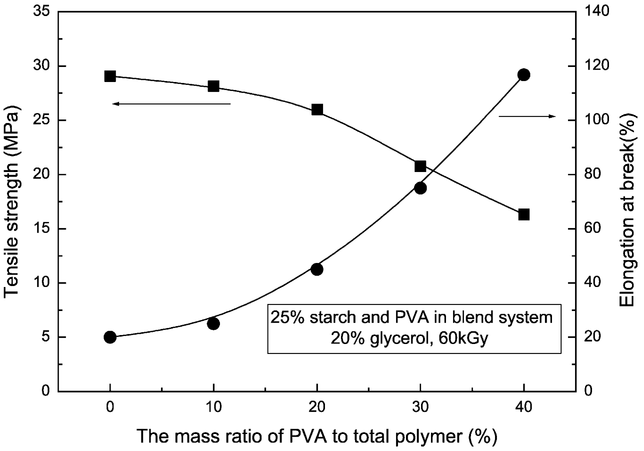


Fig. 8. The change of tensile strength and elongation at break of dry starch/PVA blend plastic sheets with the content of PVA in mixture.

PVA and starch, the tensile strength increased reasonably with dose due to the chemical crosslinking in PVA and starch mixture (the results were not shown in this paper). By the way, in our experiment condition it was also found that starch/PVA blend plastic sheet could not be prepared by compression-molding if wet starch/PVA blend plastic sheet was not irradiated. Because starch/PVA mixture were very sticky, and the mold unloading of wet starch/PVA blend plastic sheet without irradiation was impossible.

With increasing of the content of PVA, the gel fraction and water absorption of starch/PVA blend plastic sheets increased slightly. (Fig. 9). The former is because the radiation crosslinking of PVA macromolecules is easier than that of starch molecules. The latter attribute to the hydrophilism of PVA. It is very interested that after blending with PVA, water resistance of starch-based plastic sheets was improved obviously, too. Both of tensile strength and elongation at break of wet starch/PVA blend sheets (after dry starch/PVA blend sheets absorbing water for 24 h) increased obviously with increasing of the content of PVA (Fig. 10), which indicated that the flexibility and water resistance was improved obviously after blending with PVA.

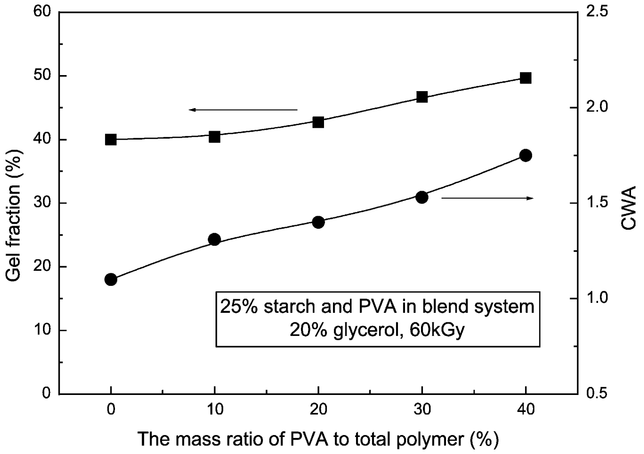


Fig. 9. The change of gel fraction and water absorption of dry starch/PVA blend plastic sheets with the content of PVA in mixture.

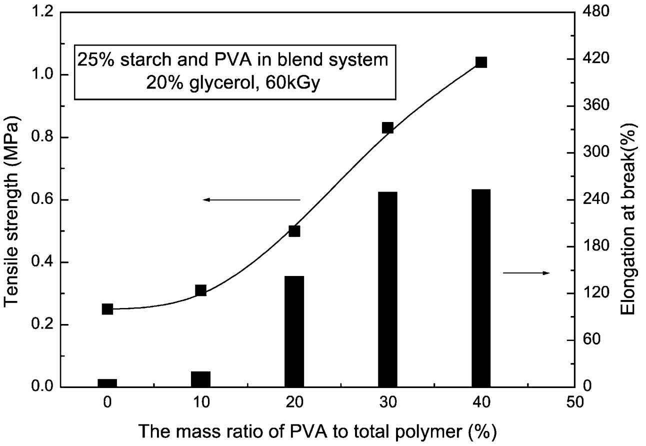


Fig. 10. The change of tensile strength and elongation at break of wet starch/PVA blend plastic sheets (after dry starch/PVA blend sheets absorbing water for 24 h) with the content of PVA in mixture.

4. Conclusion

Starch-based plastic sheets were prepared successfully by irradiation of compression-molding starch-based sheets in physical gel state.

A chemical reaction occurred during irradiation leaded to the formation of intact network structure in starch-based plastic sheets. The tensile strength of starch-based sheets was improved by radiation-induced crosslinking reaction.

The properties of starch-based plastic sheets such as flexibility (elongation at break) and wet strength was improved further by incorporating PVA into starch-based sheets under the action of ionizing radiation.

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