

Preparation of PVA/corn starch blend films and studying the influence of gamma irradiation on mechanical properties

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Abstract: In this paper, polyvinyl alcohol (PVA) /Corn Starch (CS) blend films were prepared using the solution casting method by changing the blending ratio of starch/PVA. The effects of gamma irradiation and soil burial on the biodegradability of the tested films were investigated by the mechanical properties (tensile strength and elongation to break %) and the determination of weight loss. Nevertheless, the results from the tensile strength and elongation at break tests showed that as the CS content increased, the strength decreased. After irradiation, the tensile strength and elongation to break of the films were improved the blends due to the crosslinking caused by the chemical reactions between starch macromolecules under the action of ionizing radiation. Finally, It was noticed that the weight loss increases with increasing of CS content.

Keywords: PVA, Corn Starch, Gamma Irradiation, Tensile Strength, Elongation at Break Test

1. Introduction

Developments in science and technology, especially over the last two decades, have increased the amount of synthetic polymers produced worldwide each year. Each year approximately 140 million tons of synthetic polymers are produced [1]. These artificial macromolecular substances are usually originating from petroleum and most of the conventional ones are regarded as non-degradable. However, the petroleum resources are limited and the blooming use of non-biodegradable polymers has caused serious environmental problems. In addition, the non-biodegradable polymers are not suitable for temporary use such as sutures. Thus, the polymer materials which are degradable and/or biodegradable have being paid more and more attention since 1970s [2]. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources [2].

Among the natural polymers, starch is of interest. It is considered as a suitable source material because of its inherent biodegradability, accessibility, and relatively low cost. However, the use of starch in the preparation of

starch-based biomaterials such as packaging films and agricultural plastic films is limited by its multi-hydroxyl and regular crystal structure [3]. Many efforts have been exerted to develop starch-based polymers for conserving the petrochemical resources, reducing environmental impact and searching more applications [2]. However, wide applications have been limited due to the lack of a water barrier property and poor mechanical properties, such as film brittleness caused by high intermolecular forces. Therefore, many attempts have been made to overcome these problems by blending starch with other biodegradable synthetic polymers for numerous applications [4].

Among these polymers is polyvinyl alcohol (PVA) because it is well known as a synthetic biodegradable polymer and possesses excellent mechanical properties. Its biodegradability in various microbial environments has been reported, and PVA is one of the best options to be blended with starch. Much interest lies in blending CS with PVA because CS/PVA blends have demonstrated excellent compatibility [5].

In this paper, we synthesized PVA/ CS films using a casting method. The physical properties; tensile strength (TS), elongation at fracture (E%) and the effects of gamma irradiation are investigated.

2. Experimental

2.1. Materials

The raw materials which used to prepare the films are received from the local market; CS powder, supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China), PVA water-soluble powder of molecular weight MW14000 and purity 99.9%, supplied by Merck Schuchardt OHG Hohenbrunn, Germany, Formaldehyde and Glycerin of analytical grade. The distilled and deionized waters were used.

2.2. Preparation PVA Films

PVA based biodegradable polymer films were prepared by solutions casting method. The films were prepared from 100% weight percentage ratio of PVA with a fixed formaldehyde ratio about 20%. The preparing steps can be summarized as following:

A mixture of 100 ml of deionized water and 3 ml of glycerin was prepared. PVA was mixed with the water-glycerin mixture by a shearing mixer at 500 rpm for two hours to have good homogeneity for the mixture. The temperature of the mixture was raised to 80 °C during the mixing stage. 20% weight percentage of formaldehyde was added to the mixture as plasticizer. Then the temperature of the mixture was raised to 95 °C during the mixing stage for four hours.

2.2. Preparation the CS/PVA Films

CS/PVA based biodegradable polymer films were prepared by solutions casting method. The films were prepared from different weight percentage ratios of both CS and PVA with a fixed formaldehyde ratio about 20%. The preparing steps can be summarized as following:

A mixture of 100 ml of deionized water and 3 ml of glycerin was prepared. CS and PVA polymers were weighted for suitable mixing ratios, and then mixed with the water-glycerin mixture by a shearing mixer at 500 rpm for two hours to have good homogeneity for the mixture. The temperature of the mixture was raised to 80 °C during the mixing stage. 20% weight percentage of formaldehyde was added to the mixture as plasticizer. Then the temperature of the mixture was raised to 95 °C during the mixing stage for four hours. The resulting mixture was poured on waxed glass plates of dimensions 10 × 10 cm² for casting the blend sheets. The wax was used to prevent the adhesion of composite sheets with glass plates. Then the mold was put in an oven at 50 °C for six hours for drying, and then the temperature was raised to 80 °C for one hour to get crosslinking. The sheets were pulled from the molds and cut to shapes according to the required test using a circular saw shape. The tensile test specimen is shown in Fig. 1 and the experimental ingredients used to prepare the films are shown in Table 1.



Figure 1. The shape of the tensile test specimen.

Table 1. The details of the prepared films.

Film no.	Blends ratios	Formaldehyde ratio
1	10% PVA+90% starch	Fixed ratio (10%)
2	30%PVA+70%starch	
3	50%PVA+50%starch	
4	70% PVA+30% starch	
5	90% PVA+10% starch	
6	100% PVA+0% starch	

2.3. Tensile Test Results

Tensile strength (TS) indicates the ability of a composite material to withstand forces that pull it apart as well as the capability of the material to stretch prior to failure elongation at break (EB) of the films were measured using universal testing machine type Tiniusolsen-H50KT (made in England, with full scale load capacity of 50KN). The machine is designed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous applied load and the resulting elongations using an extensometer. Crosshead speed was 10 mm/min and gauge length was 20mm. ASTM- D882 was followed for the tensile test.

2.4. Gamma Irradiation Test

The samples are irradiated to energetic γ -rays, using ⁶⁰Co gamma cell-900 of strength rate 4.5 Ci, which emits mono-energetic 1.17 and 1.33MeV γ -rays, and has a half-life of 5.3 years. The dose rate is 250 Gy/hr. The samples to be irradiated were placed in a special chamber which can be led inside the source by special electromechanical remote control. The test samples were irradiated up to accumulated dose 95kGy.

2.5. Soil Burial Test

Samples of dimensions 2×2 cm² were buried in a pot contains soil at a depth of 10 cm. The pot was placed in the laboratory, and the moisture of the soil was maintained by sprinkling water at regular time intervals. The excess water was drained through a hole at the bottom of the pot.

The degradation of the samples was determined for regular time intervals (7 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. The sample was dried until a constant weight was obtained. Weight loss of the sample over time was used to indicate the degradation rate of the soil burial test. Finally, one must be indicated that this test hold for samples without irradiation of gamma rays.

3. Results and Discussion

3.1. Tensile Properties Test Results

Fig. 2 shows the variation of the tensile strength with blend ratio of PVA/CS blend films. The resulted curve of this figure shows that as the amount of CS increased the tensile strength of the films decreased accordingly. This result can be deduced to the amorphous nature of starch which has increase the brittleness and leads to a lower tensile strength of the film [6]. The pure PVA film showed the highest tensile strength at 14.03 MPa. When CS was introduced, the 70% PVA/30%CS sample gave the highest result which about 11.95 MPa compared to other PVA/CS films. The elongation at break also, which is illustrated in Fig. 3, showed the same pattern and proportions as the tensile strength graph.

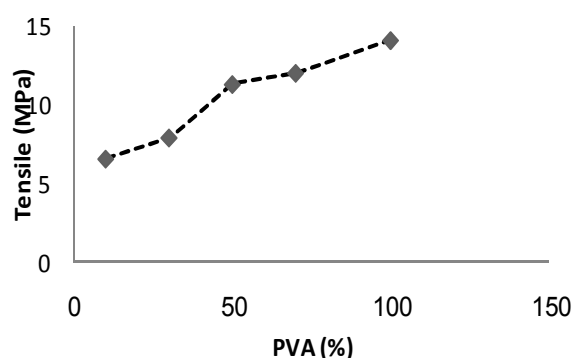


Figure 2. Effect of PVA/CS ratio on Tensile strength (with 20% formaldehyde).

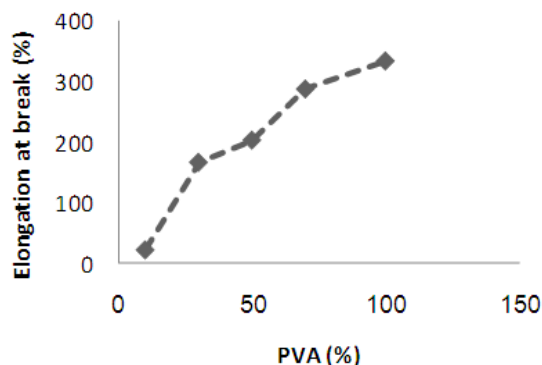


Figure 3. The effects of PVA/CS ratio on Elongation at break (%) (with 20% formaldehyde).

The percentage of elongation at break continuously decreased as the amount of CS in the matrix was increased. However, the tensile strength of the samples increased with increasing CS content. Pure PVA showed the highest percentage of elongation at break at 334.02% while the 70% PVA/30% CS film showed the maximum percentage of elongation at break at 287.83%. The smallest PVA weight percent showed the lowest percentage of elongation at break for the PVA/CS films.

The decrease in tensile strength and elongation at break with the starch is due to the amorphous nature of starch, which leads to a lower tensile strength of the films [6].

3.2. Gamma Irradiation Test Results

Fig. 4 shows the variation of tensile strength with accumulated γ -radiation dosage for the PVA/CS films to about 95 kGy. It can be noticed that the tensile strength of PVA/CS films increased with the increasing of dose. When the dose increased further, the tensile strength leveled off or decreased slightly due to degradation effect at the higher dosage [7]. The chemical reaction occurred during irradiation led to the formation of intact network structure in PVA/CS films. The tensile strength of PVA/CS films was improved by radiation-induced crosslinking reaction. However, three types of species are formed under high energy irradiation, and may become trapped in polymer, ionic species, radicals and peroxides. Both radicals and peroxides can initiate post irradiation, the various active centers, can lead to different chemical transformations such as crosslinking and degradation [8].

The interaction of radiation with matter leads to formation of positive ions and excited molecules to produce radicals. After each excitation-ionization a polymeric radical and a hydrogen atom are formed, some of those hydrogen atoms released with considerable kinetic energy in the immediate vicinity, yielding secondary polymeric radicals, pair of adjacent radicals, formed one by the radiation and the other by abstraction can then crosslink readily [9].

However, slight change of elongation at break was observed with the changing of dose, as shown in Fig. 5.

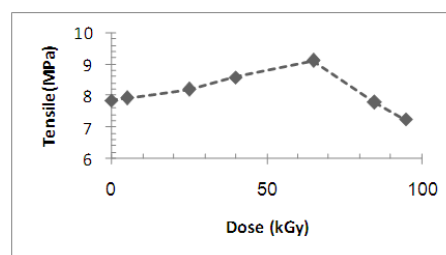


Figure 4. Variation of Tensile strength with γ -radiation dose of PVA/CS films.

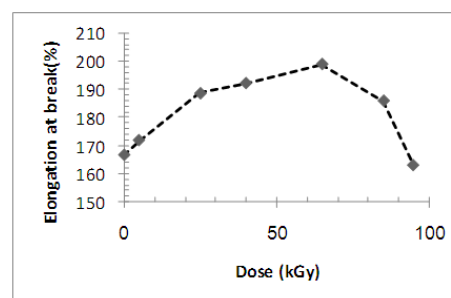


Figure 5. Variation of Elongation at break (%) with γ -radiation dose PVA/CS films.

3.3. Soil Burial Test Results

After 8 weeks of soil burial, PVA/CS films with different PVA content (10, 30, 70, and 100%) and 20% formaldehyde appeared brittle and fragile and diminished in size indicating the natural biodegradation of these films in the soil

environment. The weight losses were probably underestimated due to soil and debris adhered to the film surface [10]. Figure (6) shows the weight loss of the pure PVA and PVA/CS films soil buried for 8 weeks.

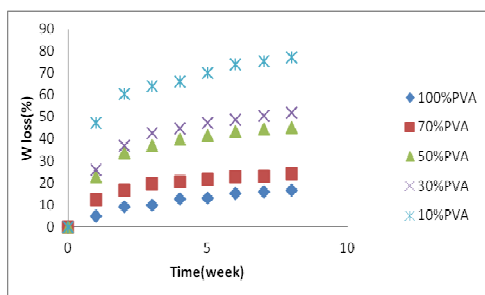


Figure 6. Weight loss of PVA/CS (with 20% formaldehyde) films after buried in soil for 8 weeks.

From Figure(6), one can be seen that all the buried films were suffered of weight loss, the weight loss increased as the burial time increased, also it can be noticed that the weight loss decrease as the PVA content increased.

All the buried films degraded rapidly in the first 7 days. This rapid degradation was due to the composting process, which occurred in two main stages: an active composting stage and a curing period. In the first stage, the temperature rose and remained elevated as long as there was available oxygen, which resulted in strong microbial activity. In the second stage, the temperature decreased but the film continued to compost at a slower rate [11].

Also Figure (6) shows that the 10% PVA / 90 % CS sample have the highest weight loss while pure PVA have the lowest weight loss over time. This finding was attributed to the corn starch content in the film which is more biodegradable than pure PVA. The PVA which is biodegradable due to its high hydrolysability, exhibited a higher resistance against soil burial degradation [12]. The higher weight loss for the pure PVA films was 77.19% after burial time in the soil for 8 weeks.

Figure (6) shows for the duration of 14 to 30 days the weight loss was slightly lower but the composting process did not stop at a particular point. Rather, it continued slowly until the last remaining nutrients were consumed by the remaining micro-organisms and almost all of the carbon had been converted into carbon dioxide [11].

4. Conclusions

The results suggested that the addition of CS to the PVA matrix reduces the brittle nature of starch and affected the degradation behavior by raising the tensile strength and elongation to break. In addition, a chemical reaction occurred during gamma irradiation led to the formation of

intact network structure in CS/PVA films. The tensile strength of CS/PVA films was improved by gamma radiation-induced crosslinking reaction. The weight loss during the buried of the films increased as the CS content increasing.

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