Radiation Modification and Characterization of Polyvinyl alcohol/Starch/Citric Acid/Glycerol Bioblend Film

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Research Article

Keywords: Radiation, Polyvinyl alcohol/Starch bioblend film, mechanical properties, thermal stability

Posted Date: March 17th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-302908/v1>

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Abstract

The blending of polyvinyl alcohol (PVA) with starch with different content of citric acid as crosslinker and glycerol as plasticizer were performed by casting method. The hydroxyl groups of PVA and Starch react with the citric acid (1 %) and glycerol (10 vol %) to form crosslinked network. The FTIR spectral analyses show the successful preparation of the different composition of the prepared PVA/ Starch /Citric acid/Glycerol bioblend films. It is found that the prepared PVA/ Starch /Citric acid/Glycerol with composition (2:1:1/10 vol %) bioblend film characterized by higher water resistance, good mechanical and higher thermal stability than other prepared bioblend films. The using of gamma radiation improved and modified water resistance property were the water uptake at equilibrium reduced remarkably at dose of 10 kGy. Also the thermal stability increased as irradiation dose increased up to dose of 30 kGy The improved mechanical and thermal properties of the selected PVA/ Starch /Citric acid/Glycerol with composition (2:1:1/10 vol %) bioblend film were compared with LDPE and PP packaging films and found to be competitive to the these commercially packaging films which are also nonbiodegradable synthetic polymers than the prepared selected PVA/ Starch /Citric acid/Glycerol with composition (2:1:1/10 vol %) bioblend film. Hence this study can be represent potential development of low cost-effective and modified PVA/ Starch /Citric acid/Glycerol with composition (2:1:1/10 vol %) bioblend film that characterized by several advantages over the commercially available petrochemical films and can be used in different applications such as packaging industry.

1. Introduction

The petroleum used synthetic polymers and its adverse effects of environmental pollution due to its limitation of recyclability and non biodegradability, promote many research on synthesis of new biodegradable renewable sources alternatives such as starch, cellulose, protein, chitin, etc due to their biodegradation and have been considered as alternatives for the nonbiodegradable petroleum based polymers [1–11].

Starch is a renewable and biodegradable polymer produced by many plants as a source of storage energy. The increasing scientific and industrial interest for starch has led to the development of numerous methods for preparing bioblends based in starch for many applications [10]. Starch has the advantage of the similarity in structure to PVA with free hydroxyl group, common solvent as water, natural tackiness and at a low price [12, 13].

Most starches in the native form present limitations such as high viscosity, susceptibility to retro gradation, limited digestibility for some, and limited solubility for others. For this reason, most starch used in Food or Industrial applications is first modified [14]. Starches are chemically and/or physically modified to accentuate their positive characteristics, diminish their undesirable qualities (such as high viscosity, susceptibility to retro gradation, and lack of process tolerance), or add new attributes (retention, film formation, digestibility, solubility, etc.) [10].

The effect of the addition of citric acid as a crosslinker for chemical modification of starch have been often used [15–17]. Citric acid can react with all three hydroxyl groups in the anhydroglucose monomer of starch and with the hydroxyl group of the reducing end of the chain cause formation of modified crosslinked starch [16].

Many techniques have been reported to improve the compatibility between PVA and starch such as addition of suitable plasticizers, cross-linking agents, fillers and compatibilizers. However, some of these crosslinking agents always display toxicity and thus their potential applications as biomaterials have been limited. To overcome these disadvantages, certain nontoxic functional additives and simple modification techniques are required to improve the mechanical properties and water resistibility of the Starch/PVA films. Citric acid (CA) is considered as safety crosslinker to improve the compatibility between PVA and starch [18].

Radiation techniques are also being successfully utilized in the preparation and production of advanced bioblends for various applications, which have contributed to a longer shelf life and a decreased incidence of contamination [5–9]. The aim of this study is to find a suitable method by using radiation technique for preparation and modification of non expansive biodegradable bioblend film to be alternatives to the petroleum synthetic polymers with good water resistance, high thermal stability and improved mechanical properties that can be applied in different fields such as packaging.

2. Experimental

Materials

PVA powder, with degree of polymerization 1700-1800, hydrolysis 98-99 % obtained from Loba Chemie (laboratory reagents and fine chemicals, India). Maize starch (amylose, 27% and amylopectin, 73%) used was supplied by the Egyptian Company for Starch and Glucose, Cairo, Egypt. Citric acid purchased from Lobachemie PVT. LTD, Mumbai, India. Glycerol 99.5 %, (Mwt = 92.09) was provided from Gomhoria pharmaceutical company, Egypt.

Preparation of Polyvinyl alcohol / starch /citric acid/glycerol bioblend film

Polyvinyl Alcohol / starch/citric acid/glycerol was prepared by dissolving 0.4 gram of PVA with 0.4 gram starch in 20 ml distilled water as a solvent and stirring at 80° C then different amounts of citric acid as a crosslinker were added separately in the different ratios of PVA: starch: citric acid 1:1:1, 2:1:1 and 2:1:2. Glycerol was added in different amounts as 10, 20, 30 and 40 vol %. The different mixtures were casted on Petri dishes of 25 cm diameter. The obtained bioblend films were left to dry at room temperature to constant weight The films were stored for 48 h before performing any testing. then the selected ratio of PVA/Starch/ citric acid/ Glycerol (2: 1:1:10 vol%) subjected to different gamma irradiation dose of 0, 2.5, 5, 10, 15, 20 and 30 kGy radiation kGy at dose rate 0.309 Gy/Sec in air using ⁶⁰Co Gamma Cell Facility of the National Center for Radiation Research and Technology, Cairo, Egypt. The formed bioblend films then cut into small films of dimension of 2 cm x 2 cm.

Characterization

Swelling behavior of Polyvinyl alcohol / starch /citric acid/glycerol bioblend film

The pre-weighted dry samples of PVA/Starch/ citric acid/ Glycerol with different contents of citric, glycerol and the irradiated selected ratio of PVA/Starch/ citric acid/ Glycerol with composition (2: 1:1:10 vol%) were immersed in deionized water for required interval at room temperature up to 72 h and quickly dried with filter paper then weighed. The swelling (%) was calculated as follow:

$$\text{Swelling (\%)} = \frac{W_s - W_o}{W_o} \times 100 \dots\dots\dots(1)$$

W_s is the weight of the sample in the swollen state and W_o is the initial weight of the dry sample

Mechanical Testing

Mechanical properties of the selected ratio of PVA/Starch/ citric acid/ Glycerol with composition (2: 1:1:10 vol%) bioblend films which irradiated at different doses of 0, 2.5, 5, 10, 15, 20 and 30 kGy radiation kGy at dose rate 0.309 Gy/Sec including tensile strength and elongation at break points were performed at room temperature using Zwick tensile testing machine Z010, Germany. The test was performed by National Standard maintained at the polymer lab. This test was carried out according to ASTM D 882-02, crosshead speed 5 mm/min using load cell of 100 N. The recorded value of the tensile strength and elongation at break is average of three measurements.

Thermal Analysis

Thermal properties of the selected ratio of PVA/Starch/ citric acid/ Glycerol with composition (2: 1:1:10 vol%) bioblend films were determined by TGA thermal analysis which carried out by using Shimadzu 24 simultaneous DTA-TGA system of type DTG-60 H (Japan). The TGA heating rate was 20 °C/min from the ambient temperature up to 600 °C and flow rate of pure nitrogen of 30 ml/min was used. The analysis was performed at the Micro-analytical center, Cairo University, Egypt

3. Results And Discussion

FTIR Spectroscopic Analysis

FTIR spectra represented in Figure 1 (a-f) corresponding to original starch, and the effect of both citric and glycerol contents on chemical structure of the prepared bioblends films. The characteristic peaks of original starch appeared at 3281 cm⁻¹ which is broad peak corresponding to hydroxyl groups. The two peaks appeared at 2974 cm⁻¹ and 1448 cm⁻¹ corresponding to C–H stretching and bending of normal alkane, respectively.

Figure 1 (b, and c) shows the FTIR spectral analysis for PVA/starch/Citric acid/Glycerol bioblend film with different content of citric acid. The characteristic peaks of the prepared PVA/ Starch /Citric acid/Glycerol bioblend film are similar to original starch but with shift and broadening of the characteristic peaks occur due to successful preparation of the PVA/starch/Citric acid/Glycerol bioblend. The overlap occurs between hydroxyl group of PVA, starch, glycerol and citric acid cause shift of the peak to be appeared around 3281 cm^{-1} . The C—H stretching and bending of normal alkane shifted to 2925 cm^{-1} and 1413.8 cm^{-1} . New peak appeared at 1713 cm^{-1} and 1413 cm^{-1} corresponding to carbonyl group of citric acid and glycerol respectively. All the intensities of characteristic peaks increased with increasing citric acid contents.

Figure 1 (b, and c) shows the FTIR spectral analysis for PVA/starch/Citric acid/Glycerol bioblend film with different content of citric acid. The characteristic peaks of the prepared PVA/starch Citric acid/Glycerol bioblend film are similar to original starch but with shift and broadening of the characteristic peaks occur due to successful preparation of the PVA/ Starch /Citric acid/Glycerol bioblend. The overlap occurs between hydroxyl group of PVA, starch, glycerol and citric acid cause shift of the peak to be appeared around 3281 cm^{-1} . The C—H stretching and bending of normal alkane shifted to 2925 cm^{-1} and 1413.8 cm^{-1} . New peak appeared at 1713 cm^{-1} corresponding to carbonyl group of citric acid. All the intensities of characteristic peaks increased with increasing citric acid contents.

In the case of FTIR analysis of the effect of glycerol content on the chemical structure of the prepared bioblend film with different glycerol content are similar to original starch but with shift and broadening of the characteristic peaks. The overlap occurs between hydroxyl group of PVA, Starch, glycerol and citric acid cause shift of the peak of OH groups to be appeared around 3278 cm^{-1} . The C—H stretching and bending of normal alkane shifted to 2931 cm^{-1} and 1414 cm^{-1} respectively. Finally the intensities of characteristic peaks increased with increasing glycerol contents. The previous FTIR analysis show also successful preparation of the PVA/starch/Starch acid/Glycerol bioblend film.

Equilibrium swelling

The effect of content of citric acid, glycerol and irradiation dose on the equilibrium swelling of PVA/ Starch /Citric /Glycerol bioblend film were shown in Figure 2 (a, b and c), respectively which calculated by equation (2) as a function of time. From Figure 3(a) it was found that the swelling behavior of PVA/ Starch /Citric/Glycerol bioblend film increased with increasing citric acid contents, this is may be due to increase the concentration of hydrophilic carboxylic groups of citric acid and higher mobility of bioblend chains occur by increasing citric content that result in high swelling behavior [19] . In the case of increasing glycerol contents in the PVA/ Starch /Citric/Glycerol bioblend film lead to increases of swelling behavior as shown in Figure 2(b). This is due to increase of concentration of hydrophilic (OH) groups resulted in more water uptake [10].

In the case of selected irradiated PVA/ Starch /Citric acid/Glycerol with composition (2:1:1/10vol %) bioblend film which selected due its lower swelling behavior is shown in figure 2 (b). It is found that there

is significant improvement in water resistance with increasing irradiation dose up to 10 kGy due to formation of crosslinked structure by gamma irradiation followed by increase in swelling (%) due to degradation occurred at high irradiation doses at 15, 20 and 30 kGy.

Mechanical Testing

Effect of irradiation dose from 0 kGy up to 30 KGy on Tensile strength and elongation (%) of the selected PVA/Starch/Citric acid/Glycerol with composition (2:1:1/10vol %) bioblend film were performed and represented in figure 3 (a, b).

The tensile strength strongly improved and modified by irradiation dose up to 10 kGy and furthermore little deterioration in elongation (%) occur. While at higher doses 15 up to 30 kGy degradation occur where tensile strength decreased and elongation (%) increased. This could be due to increase in interfacial adhesion between PVA and starch that forms crosslinked structure by gamma irradiation up to 10 kGy [5-9] followed by degradation at higher doses 15 up to 30 kGy.

Moreover, the improved and higher tensile properties of PVA/ Starch /Citric/Glycerol bioblend film with composition (2:1:1/10vol %) either blank (at dose 0 kGy) or radiation cured at dose 10 kGy were compared with commercially LDPE and PP films [5, 6, 20] at high load 100N as shown in table (1). The results demonstrated that the selected PVA/ Starch /Citric/Glycerol bioblend film with composition (2:1:1/10vol %) either blank (at dose 0 kGy) or radiation cured at dose 10 kGy it is represents a good competitive to the commercially LDPE and PP packaging films as shown in table 1. Therefore, the selected PVA/ Starch /Citric/Glycerol bioblend film with composition (2:1:1/10vol %) which irradiated at dose 10 kGy represent good competitive to the commercial plastic packaging.

Table (1) Comparison of tensile strength between the selected bioblend film PVA/Starch/ Citric acid/Glycerol (2:1:1/10vol %)with LDPE and PP films at speed 5 mm/min using high load cell of 100 N

Type of polymer	Tensile Strength
LDPE	12.0100
Polypropylene	3.1000
Selected blank bioblend film PVA/Starch/Citric acid/Glycerol (2:1:1/10vol %)at dose 0 kGy.	30.8300
Selected radiation improved bioblend film PVA/Starch/ Citric acid/Glycerol (2:1:1/10vol %)at dose 10 kGy.	45.1300

Thermal Analysis

The effect of different irradiation doses on the thermogravimetric analysis of the selected PVA/Starch/Citric/Glycerol bioblends with composition (2:1:1/10vol %) bioblend film were investigated and shown in figure 4 (a-g) and Table (1). From both TGA thermogram and Table (2) it is found that the

weight loss (%) of the selected irradiated PVA/Starch/Citric/Glycerol bioblend film is lower than that of unirradiated PVA/CMC/Citric/Glycerol bioblends as irradiation doses increased up to 30 kGy. Also, it can be seen that the T_{max} of the selected irradiated PVA/Starch/Citric/Glycerol bioblend film increases as irradiation doses increase. These results indicate that the selected irradiated PVA/Starch/Citric/Glycerol bioblends with composition (2:1:1/10vol %) are thermally more stable than that of unirradiated one up to irradiation dose of 30 kGy were the thermal stability improved and modified.

Finally, the maximum degradation temperature of the selected PVA/Starch/Citric/Glycerol bioblends with composition (2:1:1/10vol %) either blank (at dose 0 kGy) or radiation cured at dose 10 kGy were compared with commercially LDPE and PP films [10, 13, 20] as represented in table (3). The data revealed that it is characterized by good thermal properties and thermally stability with increasing irradiation dose as shown in table 2 that can be considered as a good competitive to the commercially synthetic LDPE and PP films which are also nonbiodegradable polymers than the selected prepared bioblend film.

Table (2) Effect of irradiation dose on thermal properties of selected PVA/Starch/Citric/Glycerol bioblends with composition (2:1:1/10vol %)bioblend film

Sample	Weight Loss (%)					T _{max}
	20%	40%	60%	80%	88%	
	Temperature (°C)					
0 kGy	248.5	307.9	359.8	424.2	593	316.2
2.5 kGy	250.2	307.1	358.2	423.2	595	313.1
5 kGy	243.2	299.8	348.9	416.9	592	312.3
10 kGy	244.1	308.1	352.2	423.2	599	309.3
15 kGy	237.2	302.4	353.5	418.5	597	314.1
20 kGy	237.18	307.2	362.2	426.5	598	319.2
30 kGy	247.2	309.7	365.5	430.4	600	317.4

Table (3) Comparison of maximum degradation temperature between selected bioblend film PVA/ starch /citric acid/glycerol with composition (2:1:1/10vol %)with LDPE and PP films.

Polymer	Maximum degradation temperature (°C)
LDPE	458
PP	376.9
Selected blank bioblend film selected bioblend film PVA/ starch /citric acid/glycerol with composition (1:1:1/30vol).bioblend film at dose 0 kGy.	316.2
selected bioblend film PVA/ starch /citric acid/glycerol with composition (1:1:1/30vol) at dose 30 kGy.	317.4

4. Conclusion

The results show that the properties of the selected prepared PVA/Starch/Citric acid/Glycerol with composition (2:1:1/10vol %) bioblend film were successfully prepared by casting method. The addition of citric acid as crosslinker with lower concentration 1 % and glycerol as plasticizer with concentration 10 % enhance water resistance, mechanical and thermal properties. The using of gamma irradiation improved and modified water resistance property, mechanical and thermal properties up to dose 10 kGy for mechanical properties and up to dose of 30 kGy for thermal properties. The non desirable properties of PVA such as higher solubility and its harmful environmental properties could be overcome by blending with biodegradable Starch. Therefore the selected prepared PVA/Starch/Citric acid/Glycerol with composition (2:1:1/10vol %) bioblend film characterized by several advantages over the commercially available petrochemical films and can be used in different applications such as packaging industry.

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Figures

Figure 1

FTIR analysis of (a) original starch, (b) PVA/ Starch /Citric acid/Glycerol (2:1:1/30 vol%), (c) PVA/ Starch /Citric acid/Glycerol (2:1:2/30 vol%), (d) PVA/ Starch /Citric acid/Glycerol (2:1:2/10 vol %), (e) PVA/ Starch /Citric acid/Glycerol (2:1:1/20 vol%), and (f) PVA/ Starch /Citric acid/Glycerol with composition (2:1:1/40 vol%) bioblend films.

Figure 2

Effect of time (h) on the swelling percent of PVA/Starch/ Citric acid/Glycerol bioblend film at (a) different concentration of citric acid (b) different concentration of glycerol and (c) different irradiation dose of selected PVA/CMC/Citric acid/Glycerol (2:1:1/10vol %) bioblend film.

Figure 3

Effect of irradiation dose on the mechanical properties of the selected PVA/Starch/ Citric acid/Glycerol (2:1:1/10vol %) bioblend film.

Figure 4

Effect of irradiation dose on the TGA analysis of the selected PVA/Starch/ Citric acid/Glycerol (2:1:1/10vol %) bioblend film. bioblend film at different irradiation doses (a) 0 kGy, (b) 2.5 kGy, (c) 5 kGy, (d) 10 kGy, (e) 15 kGy, (f) 20 kGy and (g) 30 kGy.