Radiation modification and characterization of polyvinyl alcohol/starch/citric acid/glycerol bioblend film

Ashraf M Abdel-Ghaffar¹ and Hussein E Ali²

Abstract
Blend films of polyvinyl alcohol (PVA) with starch (St) were obtained by casting method. The effect of different contents of glycerol (Glyc) and citric acid (CA) was investigated. The successful preparations of different compositions were shown by FTIR analysis. The bioblend film of PVA/St/CA/Glyc with a composition of (2:1:1/10 vol %) was selected due to its water resistance, higher mechanical properties, and good thermal stability than other prepared bioblend films. Further improvements were obtained by irradiation with gamma rays at a dose of 10 kGy, where the water resistance was highly reduced and the tensile strength strongly improved. The thermal stability increased with the increasing of irradiation doses up to 30 kGy. The modified thermal and mechanical properties of the selected film either non-irradiated or irradiated were compared with widely used commercially packaging films such as LDPE and PP films. Compared to commercially packaging films, the selected PVA/St bioblend film has higher tensile properties, good and closely thermal properties either non-irradiated or irradiated one. Hence, the study showed the development of modified PVA/St bioblend film, which can be used in many fields such as the packaging industry.

Keywords
Gamma radiation, polyvinyl alcohol/starch bioblend films, mechanical tests, thermal properties, packaging

Received 4 January 2022; accepted 5 August 2022.

¹Radiation Research of Polymer Chemistry Department, Industrial Irradiation Division, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority, Cairo, Egypt
²Radiation Chemistry Department, Radiation Research Division, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority, Cairo, Egypt

Corresponding author:
Ashraf M Abdel-Ghaffar, Radiation Research of Polymer Chemistry Department, Industrial Irradiation Division, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority P.O. Box 29, Cairo, Egypt.
Email: am_abdelghaffar@yahoo.com
Introduction

The petroleum origin polymers have harmful effects on the environment due to their non-biodegradability and difficulty of recycling processes. Thus, various research studies were conducted on the preparation of naturally based, new renewable, and biodegradable polymers such as cellulose,\textsuperscript{1} chitosan,\textsuperscript{2} starch (St),\textsuperscript{3,4} and CMC,\textsuperscript{5} which are considered alternatives to the petroleum origin polymers\textsuperscript{6–9} and can be applied in different fields.\textsuperscript{10–13}

Starch is natural abundant and biodegradable polymer produced by plants as an energy storage source. Most natural starches have limited applications due to their high viscosity, limited solubility, limited digestibility, and susceptibility to retrogradation for others. For these reasons, considering, starches should be modified before using in the most food and industrial applications.\textsuperscript{14} This led to the development of many preparation methods for bioblend polymers based on St which can be used in many applications.\textsuperscript{10}

Polyvinyl (PVA) has been utilized in the commercial packaging industry due to its excellent film-forming ability, biodegradability, and optical properties but still suffer high water solubility, low tensile strength, and a high degree of water absorption.\textsuperscript{8} These disadvantages can be overcome by fabrication of polymer blends with crosslinked materials to obtain the ideal properties of the film.

Polyvinyl alcohol and St have similar chemical groups, but PVA is easily dissolved in water.\textsuperscript{15,16} Various preparation techniques were investigated to improve the compatibility between St and PVA by adding of crosslinking agents, plasticizers, compatibilizers, and other fillers.

The employing of citric acid (CA) as a crosslinking agent to St for chemical crosslinking modifications is widely used by many researchers.\textsuperscript{17–19} In our study, CA was used as a crosslinking agent to the PVA/St blend of to improve their compatibility and obtain crosslinked bioblend. The carboxylic groups (-COOH) of CA react with all hydroxyl groups (-OH) in the anhydroglucose monomer of St and PVA causing the formation of a chemically modified and crosslinked structure.\textsuperscript{20} Also, CA is considered as a safe crosslinker and has non-toxic effect that obtained from a natural source and can modify the compatibility and crosslinking between PVA and St.\textsuperscript{20}

Glycerol (Glyc) is the most used plasticizer due to its good plasticization efficiency, large availability, and low exudation.\textsuperscript{21} Glycerol can be used to modify the compatibility and crosslinking between PVA and St.

The novelty of this work is to use of gamma irradiation as a successful technique to induce further modification\textsuperscript{5–9,22} of the prepared bioblend film without adding of any toxic additives as in other ordinary chemical techniques. The prepared bioblend films which modified by gamma radiation technique will have a long shelf life and be sterilized in one step.\textsuperscript{5–9} Moreover, the water resistance and mechanical properties of the selected irradiated PVA/St bioblend film will be further modified through crosslinking by gamma radiation.\textsuperscript{5–7} Therefore, it is expected that the non-expensive PVA/St bioblend films could be alternatives to the synthetic origin polymers, where can be applied in many fields such as the packaging industry.\textsuperscript{10–13,23}

Materials and methods

Materials

Polyvinyl alcohol with degree of hydrolysis 98–99% and has DP 1700–1800 was provided from Loba Chemie (laboratory reagents and fine chemicals, India). Maize St (amylopectin 73% and amylose 27%) was purchased from the Egyptian Company for St and Glucose, Cairo, Egypt.
Glycerol 99.5% (Mwt = 92.09) was obtained from Gomhoria Pharmaceutical Company, Egypt. Citric acid was obtained from Lobachemie PVT. LTD, Mumbai, India.

**Synthesis of PVA/St bioblend film**

The PVA/St bioblend films were prepared by mixing 0.4 g of PVA with 0.4 g of St and dissolved in 20 mL distilled water with stirring at 80°C. Different contents of CA as a crosslinker were added separately into the PVA/St/CA films with different compositions of (1/1/1), (2/1/1), and (2/1/2). Glycerol was also added in different contents of 10, 20, 30, and 40 vol% with respect to the weight of both PVA and St.5–7 After complete dissolution, the different compositions were cast on Petri dishes with a diameter of 25 cm. The prepared PVA/St bioblend films were dried to constant weight at room temperature. The selected PVA/St/CA/Glyc (2:1:1:10 vol%) [PVA/St bioblend film] with an average thickness of 0.16 mm was irradiated with gamma rays at different doses of 0, 2.5 kGy, 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy in air. The dose rate was 0.309 Gy/Sec was carried out using 60Co source. The gamma cell facility used was located at the National Center for Radiation Research and Technology, Cairo, Egypt. The obtained bioblend films were cut into small films with a dimension of 2 cm x 2 cm.

**Characterization**

*FTIR spectroscopic analysis.* The infrared spectroscopic analysis of the different compositions of the prepared bioblend film was carried out in the range of 400–4000 cm⁻¹ using Fourier transform infrared spectroscopy FTIR-Vertex 70 spectrophotometer, Bruker, Germany.

*Equilibrium swelling.* The pre-weighted and dried blank PVA/St bioblend films with different contents of CA and Glyc as well as the selected irradiated PVA/St bioblend films were immersed in deionized water up to 72 h at room temperature then quickly dried with filter paper and weighed until reaching equilibrium swelling. The equilibrium swelling (%) was determined by equation (1)⁵⁻⁹

\[
\text{Equilibrium swelling (\%)} = \frac{W_s - W_o}{W_o} \times 100
\]  

(Wₚ is the weight of the bioblend films after swelling, and Wₒ is the initial weight of the dried bioblend films.

*Mechanical tests*  
Tensile strength and elongation at break points (%) of the selected PVA/St bioblend film which were irradiated by gamma rays at different doses 0, 2.5, 5, 10, 15, 20, and 30 kGy at a dose rate of 0.309 Gy/Sec were determined at room temperature using Zwick tensile testing machine Z010, made in Germany. The analyses were performed at the National Institute of Standards. These tests were carried out according to ASTM D 882–02, where the crosshead speed was 5 mm/min, and a load cell of 100 N. The obtained elongation at break (%) and tensile strength values are the average of the measured three bioblend films.
Thermal analysis

Shimadzu 24 simultaneous DTA-thermogravimetric analysis (TGA) system of type DTG-60 H made in Japan was used for thermal analysis of the selected PVA/St bioblend film. The TGA heating rate was 20°C/min from the ambient temperature up to 600°C and the flow rate of pure nitrogen was 30 (ml/min) was used. The analyses were performed at the Micro-analytical Center, Cairo University, Egypt.

Scanning electron microscopy

EISS- EVO 15 Scanning electron microscopy (SEM) made in the United Kingdom was used to investigate the morphology of the surfaces of the selected PVA/St bioblend film at different doses. A sputter coater was used to pre-coat conductive gold onto the fracture surfaces for 6 min before observing the micrographs at EHT = 7.00 Kv and magnification of 1.50 KX.

Results and discussion

FTIR analysis

Figure 1(a) to (f) presents the FTIR spectral analysis of the original St, and the prepared bioblend films containing different contents of CA, and Glyc. For the original St the characteristic peak appeared at 3281 cm$^{-1}$, which corresponds to the OH groups and the two peaks appeared at 2974 cm$^{-1}$ and 1342 cm$^{-1}$ correspond to stretching and bending of the C—H groups, respectively. The peak appeared around 1639 cm$^{-1}$ corresponds to -OH bending. The major adsorption bands in the region 1249-1000 cm$^{-1}$, arising from C-O, C-C, and C-O-H stretching and C-O-H bending.

The FTIR spectral analyses for the PVA/St/CA/Glyc bioblend film with different contents of CA are shown in Figure 1(b) and (c). The characteristic peaks are similar to that of the original St but with shifting in positions and broadening of the characteristic peaks. This is due to the successful synthesis of the PVA/St bioblend films with different contents of CA. The overlap occurs between the hydroxyl groups of PVA, St, Glyc, and CA causing the position of the peak to shift at 3291 cm$^{-1}$. Also the C-H stretching and bending of C-H groups peak was shifted to 2927 cm$^{-1}$ and 1408 cm$^{-1}$, respectively. In addition, a new peak appeared at 1709 cm$^{-1}$ which corresponds to the carbonyl groups (C=O) of both CA and Glyc. Moreover, the intensities of the peaks increased with increasing CA contents as shown in Figure 1(b) and (c).

FTIR analyses of the prepared PVA/St films with different contents of Glyc are similar to those of the original St but with shifting in position and broadening of the characteristic peaks. Overlap occurred between peaks of the OH groups of PVA, St, CA, and Glyc which causing the position of the peak of OH groups to shift and appeared at 3280 cm$^{-1}$.

Moreover, the C-H stretching and bending were shifted to 2933 cm$^{-1}$ and 1414 cm$^{-1}$, respectively. In addition, a new peak appeared at 1713 cm$^{-1}$ which correspond to the carbonyl groups (C=O) of both CA and Glyc. By increasing contents of Glyc, the intensities of the characteristic peaks were increased. Finally, the FTIR analysis showed the successful fabrication of the PVA/St bioblend films with different contents of the CA and Glyc.
Figure 1. FTIR analysis of (a) original starch, (b) PVA/St/CA/Glyc (2:1:1/30 vol%), (c) PVA/St/CA/Glyc (2:1:2/30 vol%), (d) PVA/St/CA/Glyc (2:1:2/10 vol%), (e) Selected PVA/St bioblend film, and (f) PVA/St/CA/Glyc with composition (2:1:1/40 vol%) bioblend films.
**Equilibrium swelling**

The equilibrium swelling of the PVA/St bioblend films with different contents of CA and Glyc, and the effects of different irradiation doses of 0, 2.5 kGy, 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy on the swelling behavior are shown in Figure 2(a) to (c). From Figure 2(a), the swelling behavior of the PVA/St film increased with increasing the CA contents.

This is due to the increase of CA’s hydrophilic carboxylic groups (–COOH), and the high mobility of the bioblend chains that occur by increasing the CA contents which cause a high swelling behavior and low water resistance. Additionally, increasing the Glyc contents led to increase in swelling (%). This is due to increasing the contents of the hydrophilic hydroxyl groups (OH) of Glyc resulting in more water uptake up to 30% Glyc content. This followed by slight dissolution and degradation of the film at a high Glyc content of 40%. Since the Glyc molecules are small, they present high capability to interact with PVA and St chains, hence enhancing the molecular mobility. This increases the free volume in the film matrix with consequently increasing the water molecules absorbed and degradation of the film occurs.

Therefore, by changing in the compositions of the prepared bioblend films with different contents of CA and Glyc, the swelling behavior was reduced from 317% to 116% for the selected blank PVA/St/CA/Glyc bioblend film with composition of (2:1:1/10vol %).

Figure 2(c) shows the effect of irradiation doses of 0, 2.5 kGy, 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy on the swelling behavior of the selected PVA/St bioblend film.

The PVA/St bioblend film, which was modified at a dose of 10 kGy, was selected due to its higher water resistance behavior than other bioblend films with different compositions.

It is found that the water resistance significantly improved with increasing irradiation dose up to 10 kGy due to the formation of crosslinked structure by gamma rays. The swelling behavior was reduced from 116% for the selected blank PVA/St bioblend film to 97% for the radiation modified one at a dose of 10 kGy as shown in Figure 2(c). This is probably due to the increase in interfacial adhesion forces between PVA and St at an irradiation dose of 10 kGy that the crosslinked structure formed via formation of covalent bonds.

At higher doses of 15 kGy up to 30 kGy, the increase in swelling behavior occurred. This is due to degradation of the bioblend films at these higher irradiation doses.

Therefore, it could be observed from Figure 2(a) to (c) that the content of the CA should not exceed 1%, the Glyc content should not exceed 10 vol%, and the best irradiation dose is 10 kGy to obtain bioblend film with lower swelling behavior that has good water resistance.

Finally, the selected radiation modified PVA/St bioblend film at a dose of 10 kGy did not show any sign of degradation within the studied swelling period up to 72 h. Moreover, after its end of life, the ordinary water in soils will facilitate biodegradation, which is an exciting attribute for environmental sustainability.

**Mechanical tests**

Figure 3(a) and (b) illustrates the effect of irradiation doses of 0, 2.5 kGy, 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy on the mechanical properties (the tensile strength and elongation at break (%)) of the selected PVA/St bioblend film.
Figure 2. Effect of time (h) on the swelling percent of PVA/St/CA/Glyc bioblend films at (a) different concentration of CA, (b) different concentration of Glyc, and (c) different irradiation doses of the selected PVA/St bioblend film.
The tensile strength significantly modified and improved at an irradiation dose of 10 kGy accompanied with little elongation (%) deterioration. However, at higher doses of 15 kGy up to 30 kGy, the tensile strength decreased and elongation (%) increased.

This is probably due to the increase in interfacial adhesion forces between PVA and St at an irradiation dose of 10 kGy that the crosslinked structure formed via the formation of covalent bonds. At higher gamma irradiation doses of 15 kGy, 20 kGy, and 30 kGy, poor mechanical properties occurred due to the degradation at those higher doses where lower tensile strength was observed.

Moreover, the improved tensile strength of the selected PVA/St bioblend film either blank or modified at the irradiation dose of 10 kGy were compared with those of LDPE and PP which are widely used commercial films as shown in Table 1. The results showed that the selected bioblend film is characterized by higher tensile properties due to the presence of the CA as a good crosslinker, hydrogen bonding formed with Glyc, and further modification obtained at a dose of 10 kGy resulting in formation of stronger and more flexible material. This indicates that the selected PVA/St bioblend film represents a good competitor to the LDPE and PP commercial packaging films.

**Thermal analysis**

The thermal analysis is important in deciding the manufacturing and processing temperature without material degradation process. The thermal stability of the selected PVA/St bioblend film is
important in determining of their processing conditions and their further applications. Therefore, to identify whether the radiation effect can help to improve the thermal stability or not, the TGA was investigated. Table 2 and Figure 4(a) to (g) show the effect of various irradiation doses of 0 kGy, 2.5 kGy, 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy on the thermal properties of the selected PVA/St bioblend film.

From TGA analysis of the selected PVA/St bioblend film as shown in Figure 4(a) to (g), there are 4 heat degradations stages. The first stage in the temperature found in the range of 44–172°C corresponds to elimination of moisture. The second and the third stage is in the temperature range of 172–264°C and 264–376°C; these correspond to the pyrolytic decomposition of C-C and C-O, respectively, of the PVA, and St side chains. This result in the evolution of decomposition products including carbon dioxide, carbon monoxide, water, and volatile organic compounds, followed by degradation of residue which was attributed to the cleavage of the C-C backbone of the polymer, that is, so-called carbonization in the fourth stage 376–491°C.

From TGA analysis of the selected PVA/St bioblend film as shown in Figure 4(a) to (g), there are 4 heat degradations stages. The first stage in the temperature found in the range of 44–172°C corresponds to elimination of moisture. The second and the third stage is in the temperature range of 172–264°C and 264–376°C; these correspond to the pyrolytic decomposition of C-C and C-O, respectively, of the PVA, and St side chains. This result in the evolution of decomposition products including carbon dioxide, carbon monoxide, water, and volatile organic compounds, followed by degradation of residue which was attributed to the cleavage of the C-C backbone of the polymer, that is, so-called carbonization in the fourth stage 376–491°C.

From Figure 4(a) to (g) and Table 2, the weight loss (%) of the radiation modified PVA/St film is lower than that of the unirradiated film up to 30 kGy. Furthermore, the $T_{\text{max}}$ of the selected irradiated modified bioblend film significantly increased with the increase of irradiation doses. This shows that the selected PVA/St bioblend film was modified by radiation since the thermal properties were improved at a dose of 10 kGy.

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

Table 1. Comparison of tensile strength between the selected PVA/St bioblend film with LDPE and PP films at a speed of 5 mm/min using high load cell of 100 N.

| Type of polymer | Tensile strength (MPa) |
|----------------|------------------------|
| LDPE           | 12.0100                |
| Polypropylene  | 3.1000                 |
| Blank selected PVA/St bioblend film at dose of 0 kGy | 28.80 |
| Selected irradiated PVA/St bioblend film at dose of 10 kGy | 33.78 |

Table 2. Effect of irradiation dose on thermal properties of the selected PVA/St bioblend film.
Figure 4. Effect of irradiation dose on the TGA analysis of the selected PVA/St 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.
The maximum degradation temperature of the selected bioblend film either blank (dose 0 kGy) or modified at a dose of 10 kGy was compared with commercial packaging films, LDPE, and PP. In addition, the maximum degradation temperature of the selected PVA/St bioblend film was compared with the selected PVA/CMC bioblend film which is successfully prepared by the same authors as shown in Table 3.

It is observed that the selected bioblend film has decent and close thermal properties compared to commercial packaging films (LDPE and PP). Moreover, the selected PVA/St bioblend film is more thermally stable than the selected PVA/CMC bioblend film which is successfully prepared by the same authors. This is due to the presence of CA as a good crosslinker, more hydrogen bonding formed between PVA/St and Glyc and the further modification obtained by radiation crosslinking with gamma rays at a dose of 10 kGy. Therefore, the selected bioblend film can be considered competitive to petroleum origin synthetic films such as LDPE and PP films, which are nonbiodegradable polymers compared to the selected prepared biofilm.

### Table 3. Comparison of maximum degradation temperature between selected PVA/St bioblend film with LDPE and PP films.

| Polymer                                           | Maximum degradation temperature (°C) |
|---------------------------------------------------|-------------------------------------|
| LDPE                                              | 458                                 |
| PP                                                | 376.9                               |
| Selected blank bioblend film PVA/CMC at dose of 0 kGy | 278.8                               |
| Selected radiation improved bioblend film PVA/CMC at dose of 10 kGy | 280                                |
| Blank selected PVA/St bioblend film at a dose of 0 kGy | 316.2                               |
| Selected irradiated PVA/St bioblend film at a dose of 10 kGy | 317.4                               |

Scanning electron microscopy

Figure 5(a) to (g) presents the SEM photos that show the effect of different irradiation doses of 2.5 kGy, 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 30 kGy on the surface morphology of the selected PVA/St bioblend film. From Figure 5(a) which corresponds to the surface morphology of the original bioblend film at 0 kGy, it had a smooth and homogeneous surface; while the morphology of the selected bioblend at doses of 2.5 and 5 kGy, the surface showed some wrinkles and globules due to chemical structure rearrangement. For the Figure 5(d) which is the surface morphology of the selected bioblend film at dose of 10 kGy, it shows homogenous and dense structure, which could be due to the increase in interfacial adhesion bonds between PVA and St by the effect of gamma irradiation that forms crosslinked structure as discussed in the previous swelling, thermal, and mechanical test studies.

At higher doses of 15, 20, and 30 kGy, which are shown in Figure 5(e) to (g), respectively, the surface contains many peeling, and globules surface owing to the degradation that occurs at those higher doses that have breaking points in the polymer matrix as discussed in the previous swelling, and mechanical analyses. Based on the SEM results, the optimum
Figure 5. Effect of irradiation dose on the SEM of the selected PVA/St bioblend films 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.
irradiation dose for modifying the chemical, mechanical, thermal and surface morphology of the selected PVA/St bioblend film is 10 kGy.

**Conclusion**

In the current study, the PVA/St bioblend films were successfully synthesized by the casting method. The use of CA as crosslinker (1 wt%) and Glyc as plasticizer (10 vol %) enhanced the water resistance, mechanical, and thermal properties. The gamma irradiation at a dose of 10 kGy further improved and modified the properties of the selected PVA/St bioblend film. The harmful environmental effect of PVA when used in large quantities and its higher solubility could be overcome by blending with biodegradable St. Moreover, the improved tensile strength and thermal stability of the selected PVA/St bioblend film, either blank or modified at an irradiation dose of 10 kGy were compared with the widely used LDPE and PP commercial films. The results showed that the selected bioblend film has higher tensile properties, good and closely thermal properties than these of commercial packaging films. Moreover, the selected PVA/St bioblend film is more thermally stable than the selected PVA/CMC bioblend film which is previously prepared by the same authors. This is due to the presence of CA as a good crosslinker, hydrogen bonding formed with Glyc and the further modification obtained by irradiation with gamma rays at a dose of 10 kGy. This indicates that the selected PVA/St bioblend film can be used in different fields such as packaging film.

**Declaration of conflicting interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

**Funding**

The author(s) received no financial support for the research, authorship, and/or publication of this article.

**ORCID iD**

Ashraf M Abdel-Ghaffar https://orcid.org/0000-0002-2228-1750

**References**

1. Vineeth SK, Gadhave RV and Gadekar PT. Nanocellulose applications in wood adhesives: review. *Open J Polym Chem* 2019; 9: 63–75.
2. Mendes JF, Paschoalin RT, Carmona VB, et al. Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion. *Carbohydr Polym* 2016; 137: 452–458.
3. Aydın AA and Ilberg V. Effect of different polyol-based plasticizers on thermal properties of polyvinyl alcohol:starch blends. *Carbohydr Polym* 2016; 136: 441–448.
4. Mittal A, Garg S, Premi A, et al. Synthesis of polyvinyl alcohol/modified starch-based biodegradable nanocomposite films reinforced with starch nanocrystals for packaging applications. *Polym Polym Compos* 2020; 29: 405–416.
5. Abdel Ghaffar AM and Ali HE. Radiation modification of the properties of polypropylene/carboxymethyl cellulose blends and its biodegradability. *Bull Mater Sci* 2016; 39: 1809–1817.
6. Ali HE and Abdel Ghaffar AM. Preparation and effect of gamma radiation on the properties and biodegradability of poly(styrene/starch) blends. *Rad Phys Chem* 2017; 130: 411–420.
7. Abdel Ghaffar AM, Ali HE, Nasef ShM, et al. Effect of gamma radiation on the properties of crosslinked chitosan nano composite film. *J Polym Environ* 2018; 26: 3226–3236.
8. Abdel Ghaffar AM, Ali HE and Maziad NA. Modification of low density polyethylene films by blending with natural polymers and curing by gamma radiation. *Polym Sci Ser B* 2019; 61: 776–784.
9. Maziad NA, Abdel Ghaffar AM and Ali HE. Polyethylene film modification using polyactic acid - starch additives and study ionizing radiation effect onto aging properties. *Environ Prog Sustain Energ* 2021; 40: e13556.
10. Le Corre D and Angellier-Coussy H. Preparation and application of starch nanoparticles for nanocomposites: a review. *React Funct Polym* 2014; 85: 97–120.
11. Tian H, Yan J, Rajulu AV, et al. Fabrication and properties of polyvinyl alcohol/starch blend films: effect of composition and humidity. *Int J Biol Macromol* 2017; 96: 518–523.
12. Shokrani H, Shokrani A, Jouyandeh M, et al. Green polymer nanocomposites for skin tissue engineering. *ACS Appl Bio Mater* 2022; 5(5): 2107–2121.
13. Vatanpour V, Gul BY, Zeytuncu B, et al. Polysaccharides in fabrication of membranes: a review. *Carbohydr Polym* 2022; 81: 119041.
14. Daniel JR, Whistler RL and Röper H. Starch. In: *Ullmann’s Encyclopedia of Industrial Chemistry*, 2007 (ed). Wiley: VCH Verlag GmbH & Co, 2000.
15. Sin LT, Rahman WAWA, Rahmat AR, et al. Detection of synergistic interactions of polyvinyl alcohol-cassava starch blends through DSC. *Carbohydr Polym* 2010; 79: 224–226.
16. Tang X and Alavi S. Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability. *Carbohydr Polym* 2011; 85: 7–16.
17. Poronsukomboona K, Holló B, Szécsényib K, et al. Properties of baked foams from citric acid modified cassava starch and native cassava starch blends. *Carbohydr Polym* 2016; 136: 107–112.
18. Menzela C, Olssonb E, Plivelic TS, et al. Molecular structure of citric acid cross-linked starch films. *Carbohydr Polym* 2013; 96: 270–276.
19. Mei J-Q, Zhou D-N, Jin Z-Y, et al. Effects of citric acid esterification on digestibility, structural and physicochemical properties of cassava starch. *Food Chem* 2015; 187: 378–384.
20. Priya B, Gupta VK, Pathania D, et al. Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulose fiber. *Carbohydr Polym* 2014; 109: 171–179.
21. Epure V, Griffon M, Pollet E, et al. Structure and properties of glycerol-plasticized chitosan obtained by mechanical kneading. *Carbohydr Polym* 2011; 83: 947–952.
22. Abdel Hakiem AA, Abdel Moneam YK, Said HM, et al. Radiation induced biodegradable polymer blends for growth promotion of corn plants. *Polym Renew Resour*. Article In press 2022.
23. Sreekumar K, Bindhu B and Veluraja K. Perspectives of polyactic acid from structure to applications. *Polym Renew Resour* 2021; 12: 60–74.
24. Wilpiszewska K, Antosik AK and Zdanowicz M. The effect of citric acid on physicochemical properties of hydrophilic carboxymethyl starch-based films. *J Polym Environ* 2019; 27: 1379–1387.
25. Mohamed R, Nurazzi NMN, Aisyah MIS, et al. Swelling and tensile properties of starch glycerol system with various crosslinking agents. *IOP Conf Series Mater Sci Eng* 2017; 223: 012059.
26. Luchesea CL, Brumb LFW, Piovesana A, et al. Bioactive compounds incorporation into the production of functional biodegradable films - a review. *Polym Renew Resour* 2017; 8: 151–176.
27. Oyeoka HC, Ewulonu CM, Nwuzor IC, et al. Packaging and degradability properties of polyvinyl alcohol/gelatin nanocomposite films filled water hyacinth cellulose nanocrystals. *J Bioreasour Bioprod* 2021; 6: 168–185.
28. Kumar KPA and Soundararajan S. Studies on the mechanical, barrier, optical, and characterization of photo-/biodegradable LDPE-PLA blend with nanoclay for packaging film application. *Polym Renew Resour* 2018; 9: 87–102.

29. Saeng-on J and Aht-Ong D. Production of starch nanocrystals from agricultural materials using mild acid hydrolysis method: optimization and characterization. *Polym Renew Resour* 2017; 8: 91–116.

30. Sangroniz A, Zhu J-B, Tang X, et al. Packaging materials with desired mechanical and barrier properties and full chemical recyclability. *Nat Commun* 2019; 10: 3559.

31. Abdel-Ghaffar A M and Ali H E. Effect of gamma radiation on the properties of novel polyvinyl alcohol/ carboxymethyl cellulose/citric acid/glycerol bioblend film. *Polym Bull* 2022; 79: 5105–5119.

32. El-Sawy NM, El-Arnaouty MB and Abdel Ghaffar AM. γ-Irradiation effect on the non-crosslinked and crosslinked Polyvinyl alcohol films. *Polym.-Plast Tech Engin* 2010; 49: 169–177.