Radiation induced biodegradable polymer blends for growth promotion of corn plants

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Abstract
A series of polymer blends based on plasticized starch (PLST), poly(vinyl alcohol), alginic acid (AG), and chitosan (CS) were prepared by solution casting. The different blends were exposed to electron beam irradiation to different doses to form hydrogels. The blends before and after electron beam irradiation were characterized in terms of gel fraction (%), swelling in water (%), FTIR spectroscopic analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and rheological measurements. As a practical application in the field agriculture, the hydrogels were used as growth promotion of corn plants. The results showed that the gel fraction was increases by increasing the ratio of PVA in the blends and was decreased by the addition of AG or CS due to the occurrence of degradation. On the other hand, opposite results was found in swelling in water. The corn plant growth indicated an improvement in corn plant height in presence of CS or AG polymers in starch (PLST), poly(vinyl alcohol) blends also, more improvement in corn plant heights in case of blends modified with MgSO₄.

Keywords
Polymer blends, electron beam irradiation, rheological properties physico-chemical properties

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Introduction

Natural polymers, such as polysaccharides, manifest properties that make them highly sought for, especially in the development of new materials for applications in various areas, like health care, agriculture, and environmental protection. The most important among these properties are their non-toxicity, biocompatibility, and biodegradability. The use of this natural and biodegradable polymer in agriculture is gaining popularity in science, particularly in the field of polymer chemistry. This has provided solutions to some problems of agriculture, which is to maximize land and water productivity without threatening the environment and the natural resources. Superabsorbent polymer hydrogel is one of potentially influence soil permeability, density, structure, texture, evaporation, and infiltration rates of water through the soils.

The essential macronutrients for the development of plants are phosphorus, nitrogen, potassium, calcium, and magnesium. Magnesium deficiency is a frequently occurring limiting factor for crop production due to low levels of exchangeable Mg in acidic soil, which negatively affects sustainability of agriculture development. However, the hazards of fertilizers to the environments have results to decrease or limit their use. It was found that nearly half of the applied nutrients are lost to the environment depending on the soil condition and method of application.

Starch is one of the most studied natural polymers due to its widespread and applications as well as to the global interest regarding renewable, cheap, and easy to process resources. The native form of starch is frequently subjected to different processing methods in order to modify its structure and thus to obtain some functional properties suitable in specific industrial applications. To improve the properties of starch, various physical or chemical modifications of starch such as blending, derivatization, and graft copolymerization have been studied. Starches are often blended with other materials to enhance their properties, blending starches aims to reduce the production cost; to improve barrier properties and dimensional stability; to decrease the hydrophilic character of starch; and increase its biodegradability.

Chitosan (1→4) linked 2-amino-2-deoxy β-D-glucopyranose) is the deacetylated derivative of chitin, the most abundant natural polymer (polysaccharide) on earth after cellulose. Chitosan occupies a special position due to its abundance, versatility, ease of modification, and unique properties including biodegradability, biocompatibility, non-toxicity, and anti-bacterial, as well as, hydrophilicity. Chitosan has been used to induce growth promotion in plants resulting in superior plant health and enhanced yields in numerous fruits and crops. Also, alginic acid, a widely used as natural polysaccharide, which is generally derived from brown seaweeds such as Kelp, Gulfweed, Ascophyllum, and Macroalgae. It can also be produced by a microbial fermentation using specialized bacteria. Authors were studied the use of alginate gels as matrices for slow release (SR) in agricultural applications.

Synthetic polymers play important role in agricultural uses as structural materials for creating a climate beneficial to plant growth, for example, mulches, shelters or green houses. Polyvinyl alcohol (PVA) is the most common kind of biodegradable synthetic polymers, due to their adjustable properties, mechanical strength, processability. A biodegradable starch/polyvinyl alcohol (PVA) blend film for coating the soluble granular fertilizer was prepared. This starch/polyvinyl alcohol (PVA blend film could biodegrade in the soil environment.

Recently, the effect of bio- and synthetic-polymers on enhancing soil physical properties and Lettuce plant production was reported. The bio-polymers (2%dextran, 3% alginate, and 3% xanthan) and the synthetic polymers (2 and 3% polyacrylamide and 2 and 3% diaper) were used. It was found that beneficial order of enhancement of soil physical and hydro-physical properties and plant production as obtained with Dextran, followed by Alginate, and Xanthan bio-polymers, while
synthetic polymers did not show such effects. A review on the Superabsorbent polymers (SAPs) showed that they are quite effective and useful in acting as a reservoir for water and some nutrients in arid and semiarid regions and application in agriculture. It was reported that the use of complex molecules based on natural biopolymer chitin and/or on its deacetylated derivative chitosan has resulted in great advantages for many users. In plants, chitin- and chitosan-based molecules are largely used as safe and environmental-friendly tools to ameliorate crop productivity and conservation of agronomic commodities. The effects of eco-friendly carbohydrate-based superabsorbent polymers on seed germination and seedling growth of maize were studied. It was found that it indicates that this SAP is not toxic to plants and can promote seed germination, and at the same time provides a possibility of replacing other substrates. Super absorbent polymers and their composites for application in agriculture was recently reported.

Radiation-based method is a “green tool” for modification of natural polymers, such as starch, cellulose, pectin, and chitosan, alginate, having advantages over conventional methods that involve chemical agents associated with environmental toxicity. Electron beam irradiation is one of irradiation methods that characterized by it fast, requires no catalysts, does not induce a major temperature increase, and offers a green technological approach for polymer modification to generate polymer-based materials with new functionalities. Irradiation process promoted the blending properties through inducing free radicals, these free radicals can enhance the phase adhesion between different polymers in blends at a boundary surfaces. This phase adhesion improves the mechanical properties of blends and can used to control the nutrient release properties of these blends. As shown above, there is no research work has been reported for using high-energy radiation for the modification of natural polymers for agriculture applications. Thus, the objective of the present work is to use radiation-based method as a “green tool” for the modification of natural polymers for agriculture applications. In this work, electron beam irradiation is used to prepare biodegradable polymer blends for growth promotion of corn plants. In this regard, blends based on plasticized starch, PVA, chitosan, or alginate was prepared at different compositions and then exposed to electron beam irradiation. The prepared blends were characterized in terms of gel percentage, swelling properties, Infra-Red Spectroscopy (FTIR), thermal properties, and rheology properties. The application of these blends in corn plants growth promotion was also investigated.

Experimental

Materials

Maize starch used throughout this study was supplied by the Egyptian Company for Starch and Glucose, Cairo, Egypt. Low molecular weight chitosan (CS) was purchased from Aldrich Company, Germany. Poly(vinyl alcohol) (PVA) is a laboratory grade in the form of powder, partially hydrolyzed (88%) and with average molecular weight (Mw) of 125,000. It was obtained from Laboratory Rasayan, India. Sodium alginate was obtained from Sigma-Aldrich Ltd. (Oakville, Ontario, Canada). Glycerol is a laboratory-grade chemical used as a plasticizer, and was supplied by El-Gomhoria Company, Cairo, Egypt. Magnesium sulfate was obtained from LOBA Chemie Company, India. The soil used in this work was collected from the local farms.

Preparation of plasticized starch

Stock solution of starch was prepared by adding required amounts of starch to 100 ml of distilled water at room temperature with stirring. When the mixture was completely suspended, the
temperature was slowly raised to 90°C with continuous stirring and glycerol was then added to the solution. The stirring was continued for 3h to reach complete gelatinization of starch.

**Preparation of plasticized starch/poly (vinyl alcohol)**

The required amount of PVA dissolved in hot water was added to the gelatinized starch. The foam was skimmed off and the solution was poured on polystyrene petri dishes and dried for 48 h at 37°C to form the desired films. The films were finally removed from the trays and placed in sealed containers at 4°C to avoid moisture exchange.

**Preparation of starch/poly(vinyl alcohol) and chitosan or alginate acid blends**

The blend of plasticized starch (PLST)/poly(vinyl alcohol) (PVA) was prepared at different ratios, followed by adding required ratio of chitosan (CS) solution or alginate (AG)solution or modified with adding 0.1M magnesium sulfate solution. The blends were then exposed to different doses of electron beam irradiation (EB).

**Electron beam irradiation**

Irradiation was carried out on the electron beam accelerator (3 MeV, 3 mA) facility installed at the National Center for Radiation Research and Technology, Cairo, Egypt. The irradiation time and the required doses were obtained by adjusting the electron beam parameters and conveyor speed.

**Gel fraction**

The gel content in the dried samples was measured by extracting the different insoluble blend hydrogels (Wo) in deionized water for 24 h at room temperature. The hydrogels were then dried at 80°C (Wd). The gel fraction (%) was calculated as follows

\[
\text{Gel content} (\%) = \left( \frac{W_d}{W_o} \right) \times 100
\]

**Swelling properties.** The dry samples (Wi) were immersed in deionized water for 24 h at room temperature and the samples were quickly dried with filter paper to remove excess water (Ws) and the swelling was calculated as follow

\[
\text{Swelling} (\%) = \left( \frac{(W_s - W_i)}{W_i} \right) \times 100
\]

**FTIR spectroscopic analysis**

FT-IR analysis was performed using a Mattson (Genisis) FTIR spectrometer manufactured by Unicam, England, over the range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹. Spectra with a high signal-to-noise ratio were obtained through the collection of 100 scans for each sample.
Thermogravimetric analysis

The thermal stability was investigated by thermogravimetric analysis. TGA studies were carried out using a Shimadzu-50 (TGA-50) at a heating rate of 10°C/min., over nitrogen atmosphere from room temperature up to 600°C.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was recorded with NETZSCH differential scanning calorimeter (DSC 204 F1 Phoenix) at a heating rate of 10°C/min., over nitrogen atmosphere from room temperature up to 300°C.

Rheological measurements

Rheological measurements were performed using a GEMINI-2 rheometer (Malvern, Bohlin Instruments, Worcestershire, UK) with parallel-plate geometry (plate diameter 25 mm). Dynamic frequency sweep tests were executed over the frequency range of 0.01–100 rad/s, and the testing temperature was set to 65°C.

Determination of growth of corn plants

Corn seeds, purchased from local supermarket, were planted in the soil. After 2 weeks, the prepared and irradiated starch blends was added as a fertilizer to the soil to enhance the plant growth. The corn plant was grown under natural light condition and was watered every other day. The growth was measured in terms of heights increase of the corn plants. The length from the top to the root to the end of the stem representing the height of the corn was measured.

Results and discussion

Gel fraction and solubility properties

Figure 1 shows the Effect of electron beam irradiation dose on the gel fraction (%) and solubility of PLST/PVA blends with AG and CS polymers at a constant ratio of 5%. It can be seen the gel percentage for PLST/PVA blends was increased with increasing irradiation dose and with increasing the PVA ratio. Upon EB irradiation of blend composites, crosslinking reactions involving the hydroxyl groups of PVA and those of PLST are occurred. This is because PVA as a vinyl polymer is a radiation crosslinkable polymer. In addition, the transfer of radicals from water radiolysis to polymers increases the concentration of radicals and thus increases the rate of crosslinking and gelation.

The presence of chitosan (CS) or alginic acid (AG) in PLST/PVA blends causes a decrease in the gel fraction. This behavior is attributed to the degradation occurs in CS or AG (degradable polymers) in the matrix upon EB irradiation.

As shown in Figure 1, on the contrary of the insoluble parts (gel), the solubility in water of PLST/PVA blends was found to decrease with increasing irradiation dose and with increasing the PLST ratio. On the other hand, for the PLST/PVA/AG blends the solubility in water was found to increase up a dose of 20 kGy and then tends to increase up to 50 kGy. However, in the case of PLST/PVA/CS
blends the solubility in water was found to increase up to 30 kGy and then tends to greatly decreases up to 50 kGy. This finding is attributed to the degradation occurs in CS at higher doses.

**Swelling in water properties**

Figure 2 shows the effect of EB irradiation dose and the blend composition on the swelling percentage (%). It can be seen that the swelling (%) for PLST/PVA blends and PLST/PVA blends
with chitosan (CS) or alginic acid (AG) blends was greatly decreased by increasing the EB-irradiation dose up to 50 kGy. In addition, at any irradiation dose, the swelling (%) was found to decrease with increasing the PVA ratio in PLST/PVA blends. However, the swelling (%) of PLST/PVA blends with AG was slightly higher than PLST/PVA blends with CS at similar conditions of irradiation dose and PVA content. This slightly increase may due to presence of acidic group, which increases the hydrophilicity of the matrix than other blends. The decrease in swelling properties due to irradiation doses is directly related to the occurrence of crosslinking in the PVA/PLST blends. In addition, this finding may be attributed to the movement restrictions in PLST molecules compared with PVA. Thus, the decrease in swelling could be explained based on crosslinking. In this contest,

![Figure 2. Effect of electron beam irradiation doses on the swelling (%) of PLST/PVA blends with AG and chitosan polymers at a constant ratio of 5%.](image)
upon crosslinking the blend become compact and thus resists the absorption of water through the blends.

**FT-IR analysis**

FTIR spectroscopy was used to verify the change in the chemical structures of PLST/PVA blends resulting from irradiation or adding polymers molecules. **Figure 3** shows the FTIR spectra of PLST/PVA blends at different ratios, before and after they had been electron beam irradiated to a dose of 50 kGy. The stretching vibration of –OH seen at 3426 cm\(^{-1}\), the intermolecular hydrogel at 1640 cm\(^{-1}\) and CH\(_2\)OH stretching vibration at 1260 cm\(^{-1}\) as well as C-O-C ring vibration at 929 and 858 cm\(^{-1}\) are the characteristic peaks of starch.\(^{23}\) For PVA, the FT-IR spectrum shows a broad band at 3000–3500 cm\(^{-1}\) due to –OH stretching, peaks at 2937 cm\(^{-1}\) and 950 cm\(^{-1}\) due to C-H and C-C stretching vibration. In addition, the region at 1200–1100 cm\(^{-1}\) (containing a number of modes) is due to the sensitive to crystallinity behavior of PVA.\(^{24}\) The broadening of the -OH peak of PVA was decreased due to the adding of PLST. This may be due to involvement of these groups in hydrogen bonding with starch. In addition, a decrease can be seen at 1715 cm\(^{-1}\) (C=O) and 1200 cm\(^{-1}\) (crystallinity).

**Figure 4** shows the FT-IR spectra of PLST/PVA blends with constant ratios of alginic acid (AG), before and after they had been electron beam irradiated to a dose of 50 kGy. It can be seen that the –OH stretching peak of PVA was shifted to higher wavenumbers. This may due to the involvement of –OH groups in network hydrogen bonding between tri-polymers; this shift is larger in case of adding AG than CS as shown schematically below. On the other hand, the peak at 1655 cm\(^{-1}\) due to the amide II was observed in the IR spectrum of ST/PVA/CS blend and a peak at 1720 cm\(^{-1}\) due to C=O in alginic acid.

**Figure 5** shows the FTIR spectra of PLST/PVA blends with constant ratios of chitosan (CS) before and after they had been electron beam irradiated to a dose of 50 kGy. It can be seen that the intensity of the –OH peak in the unirradiated PLST/PVA/CS blends was decreased after EB irradiation. This may due to two behaviors are occur in the blends by irradiation, first, the occurrence of crosslinking in PVA in the blends that restricted the formation of hydrogen bonding. Second, in case of blends, containing chitosan or alginic acid, the –OH peak was increased than in case of PLST/PVA because these polymers are degradable polymer forming extra-oxygenated groups in the matrix after irradiation.

**Thermogravimetric analysis**

Unirradiated PLST/PVA blends with AG and CS. **Figure 6** shows the TGA thermograms and the corresponding rate of thermal decomposition reaction of unirradiated PLST/PVA (80/20%) blends and its blends with a constant ratio (5%) of alginic acid (AG) and chitosan (CS). It can be seen all the blends express three stages of weight loss. The first stage is within the temperature range from room temperature up to ~250°C, which is due to the moisture vaporization and removal of compound water. The second stage (main stage), which is due to the decomposition of polymers and it was observed within the temperature range (~250–350°C). In this stage, the side chains decomposition was occurred evaporating CO\(_2\), H\(_2\)O, CH\(_4\), and NH\(_4\). The third stage of decomposition occurs within the temperature range of (350–500°C). In this stage, depolymerization and degradation of C-O-C backbone would occur. The temperatures of the maximum rate of decomposition reaction (T\(_{\text{max}}\)) of unirradiated PLST/PVA (80/20%) blend and its blends with a constant ratio (5%) of alginic acid (AG) and chitosan (CS) are shown in Table 1.
Figure 3. FTIR spectra of PLST/PVA blends at different ratios, before and after they had been electron beam irradiated to a dose of 50 kGy.

EB irradiated PLST/PVA blends with AG and CS. Figure 7 shows the TGA thermograms and the corresponding rate of thermal decomposition reaction rate of PLST/PVA (80/20%) blends before and after electron beam irradiation to different doses. Also, the TGA thermograms and the corresponding rate of thermal decomposition reaction of PLST/PVA/AG (80/15/5%) and PLST/PVA/CS (80/15/5%)
blends before and after electron beam irradiation to different doses are shown in Figures 8 and 9. It can be seen that the different irradiated blends undergo thermal decomposition stages similar to those thermal decomposition of unirradiated blends. The temperatures of the maximum rate of decomposition reaction ($T_{\text{max}}$) of unirradiated PLST/PVA (80/20%) blend and its blends with a

**Figure 4.** FTIR spectra of PLST/PVA/AG (80/15/5%) blends with different ratios of sodium alginate (AG) before and after they had been electron beam irradiated to a dose of 50 kGy.
constant ratio (5%) of alginic acid (AG) and chitosan (CS), EB irradiated to different doses is
shown in Table 1.

Based on these figures and data, the following points can be addressed:

**Figure 5.** FTIR spectra of PLST/PVA/CS (80/15/5%) blends with different ratios of chitosan (CS) before and after they had been electron beam irradiated to a dose of 50 kGy.
Figure 6. TGA thermograms and the corresponding rate of thermal decomposition reaction of unirradiated PLST/PVA (80/20%) blends and its blends with a constant ratio (5%) of sodium alginate (AG) and chitosan (CS).

Table 1. Temperatures of the maximum rate of decomposition reaction ($T_{max}$) of PLST/PVA (80/20%) blend and its blends with a constant ratio (5%) of sodium alginate (AG) and chitosan (CS), before and after they had been EB irradiated to different doses.

| Blend composition | Doses (kGy) | $T_{1max}$ (°C) | $T_{2max}$ (°C) |
|-------------------|-------------|-----------------|-----------------|
| PLST/PVA          | 0           | 316.7           | 496.2           |
|                   | 20          | 317.0           | 488.0           |
|                   | 50          | 313.0           | 485.0           |
| PLST/PVA/CS       | 0           | 322.7           | 502.6           |
|                   | 20          | 306.0           | 526.0           |
|                   | 50          | 307.0           | 581.0           |
| PLST/PVA/AG       | 0           | 319.0           | 519.0           |
|                   | 20          | 313.0           | 490.0           |
|                   | 50          | 316.0           | 486.0           |
Addition of CS and AG to PLST/PV A blend does not change the thermal decomposition stages of the polymer blends, however, some improvement in third decomposition step to higher $T_{\text{max}}$.

Addition of CS and AG to PLST/PVA blend was slightly decreased the $T_{\text{max}}$ of second stage and this may be due to that these polymers containing side chains easily decomposed.

EB-irradiation up to 50 kGy increases the $T_{\text{max}}$ of the third stage and this due to crosslinking that may occur between polymer chains and restricted backbone decomposition.

**Differential scanning calorimetry**

Figures 10 and 11 show the DSC thermograms of PLST/PV A (80/20%) blends before and after electron beam irradiation to different doses. A broad endothermic peak around (80–200°C) can be seen for PLST/PVA (80/20%). This peak was accompanied with a weight loss of 10% as seen in the TGA thermograms as shown in Figure 6. In this range, the thermal energy absorbed is required to gelatinization of starch molecules and/or removal of absorbed water molecules. An endothermic peak was observed at about 260°C for PLST/PVA that may be attributed to crystalline melting temperature ($T_{\text{m}}$). This peak could be compared with the stage of temperature, in which...
12% weight loss that support the idea that it is crystalline melting temperature not decomposition process. Table 2 shows the parameters of DSC measurements. EB-irradiation to a dose of 50 kGy does not have big changes of the thermograms shape with some changes in DSC parameters.

**Rheological properties**

Rheology experiments were done to investigate the structure-property relationship for PLST/PVA blends in the presence of CS or AG before and after EB irradiation to a dose of 50 kGy. Figures 12, 13, and 14 show the rheological parameters of elastic modulus ($G'$), viscous modulus ($G''$) and complex viscosity ($\mu$) for PLST/PVA (80/20%), PLST/PVA/CS or PLST/PVA/AG blends before and after they had been EB irradiated to a dose of 50 kGy. The relation between storage modulus ($G'$) concerns the storage energy of mechanical behavior and represents the elastic components in the polymer, the loss modulus ($G''$), that concerns the loss energy at mechanical behavior and represent the viscos component in the polymer, and complex viscosity ($\mu$) during applied frequencies at a temperature of (65°C). As shown in Figure 12, the parameters $G'$, $G''$ and $\mu$ for PLST/PVA showed large difference between $G'$ and $G''$ during the measuring frequency range with continuous decrease in complex viscosity. This behavior may be due to that the measurements were
Figure 9. TGA thermograms and the corresponding rate of thermal decomposition reaction of PLST/PVA/CS (80/15/5%) blends before and after electron beam irradiation to different doses.

Figure 10. DSC scans thermograms of unirradiated PLST/PVA blends and with 5% sodium alginate (AG) or chitosan (CS).
carried out at a temperature around the gelatinization temperature of starch. On the other hand, 50kGy EB-irradiated sample the $G'$ and $G''$ during the measuring frequency range were have similar trends whereas, the viscosity changed to Newtonian behavior with irradiation. The relation between viscous modulus and elastic modulus (Cole–Cole plot) is an important in investigating the molecular parameters of the prepared blends, that is, chain branching, molecular weight and molecular weight distribution) as shown in Figure 12(c). It can be seen there is a linear relation between viscous and elastic moduli for blend irradiated to 50 kGy, whereas non-irradiated blend had not linear relation. The linearity indicated similarity between the molecules after irradiation due to molecular bonding between different components. The effect of adding chitosan to the PLST/PVA blend, the viscous modulus ($G''$) had a higher values than elastic modulus ($G'$), due to the presence of chitosan working as lubricant to the blend at working temperature (65°C) and at all frequencies as shown in Figure 13. This situation is changed after EB-irradiation (Figure 13(b)). This due to the interaction occurred between different blend components through free radical interaction between these components. Also, addition of alginic acid (AG) that containing active group of (-COOH) that can form bonds between blend components that made elastic modulus higher than viscous modulus in unirradiated and irradiated samples.

**Figure 11.** DSC thermograms of EB-irradiated PLST/PVA/blends.

**Table 2.** DSC parameters of PLST/PVA (80/20%) blend and its blends with a constant ratio (5%) of sodium alginate (AG) and chitosan (CS), before and after they had been EB irradiated to different doses.

| Blend composition | Doses (kGy) | $T_g$ (°C) | $T_{1m}$ (°C) | $T_{2m}$ (°C) |
|-------------------|-------------|------------|--------------|--------------|
| PLST/PVA          | 0           | 112.8      | 189.5        | 267.8        |
|                   | 50          | 164.0      | 184.0        | 254.0        |
| PLST/PVA/CS       | 0           | 126.2      | 182.5        | 257.0        |
|                   | 50          | 151.2      | 181.2        | 345.0        |
| PLST/PVA/AG       | 0           | 162.0      | 195.1        | 258.9        |
|                   | 50          | 166.8      | 177.0        | 228.1        |
Figure 12. Rheological parameters of elastic modulus ($G'$), viscous modulus ($G''$) and complex viscosity ($\mu$) for PLST/PVA (80/20%) before and after they had been EB irradiated to a dose of 50 kGy: (A) Unirradiated, (B) 50 kGy and (C–D) Elastic modulus versus viscous modulus (Cole–Cole plot).
Figure 13. Rheological parameters elastic modulus ($G'$), viscous modulus ($G''$) and complex viscosity ($\mu$) for PLST/PVA/CS (80/15/5%) before and after they had been EB irradiated to a dose of 50 kGy: (A) Unirradiated, (B) 50 kGy and (C–D) Elastic modulus versus viscous modulus (Cole–Cole plot).
Figure 14. Rheological parameters elastic modulus (G’), viscous modulus (G’’) and complex viscosity (µ) for PLST/PVA/AG (80/15/5%) before and after they had been EB irradiated to a dose of 50kGy: (A) Unirradiated, (B) 50 kGy and (C–D) Elastic modulus versus viscous modulus (Cole–Cole plot).
The effect of chitosan (CS) and alginic acid (AG) addition to the blends on their rheological properties is seen in Figures 13 and 14. It shows that the viscous modulus is higher than elastic modulus in case of unirradiated sample.

**Figure 15.** Effects of PLST/PVA (85/15%) blends on corn plant growth: (A) PLST/PVA (0 kGy), (B) PLST/PVA (50 kGy), (C) PLST/PVA/CS (0 kGy), (D) PLST/PVA/CS (50 kGy) and (E) PLST/PVA/AG(0 kGy), (F) PLST/PVA/AG(50 kGy).

The effect of chitosan (CS) and alginic acid (AG) addition to the blends on their rheological properties is seen in Figures 13 and 14. It shows that the viscous modulus is higher than elastic modulus in case of unirradiated sample.
Table 3. The effect of PLST/PVA (85/15%) blends with CS and AG on corn plant growth in terms of the heights, in which the planting soil was mixed with the modified blends before and after EB irradiation to a dose of 50 kGy.

| Blend composition       | Doses (kGy) | Mg$^{+2}$ | Height of plant (cm) |
|-------------------------|-------------|-----------|----------------------|
| PLST/PVA (85/15%)       | 0           | 0         | 29                   |
|                         | 50          | 0         | 40                   |
| PLST/PVA/CS (80/15/5%)  | 0           | 0         | 49                   |
|                         | 50          | 0         | 54                   |
|                         | 50          | ++        | 90                   |
| PLST/PVA/AG (80/15/5%)  | 0           | 0         | 46                   |
|                         | 50          | 0         | 50                   |
|                         | 50          | ++        | 90                   |
| PLST/PVA/CS (80/15/5%)  | 50          | 0         | 50                   |
| PLST/PVA/CS (80/5/15%)  | 50          | 0         | 60                   |

Figure 16. Effects of chitosan concentration on plant heights: (A) PLST/PVA/CS (5%) and (B) PLST/PVA/CS (15%).

Effect of PLST/PVA blends on corn plant growth

In the in absence of magnesium. In this experiment, the unirradiated or EB irradiated PVA/PLST blends with CS or AG, as green materials, was mixed with the soil in corn planting. Figure 15 shows the effect of PLST/PVA (85/15%) blends with CS or AG on corn plant growth before and after EB irradiation to a dose of 50 kGy. Table 3 shows the corn plant heights after the planting in soil mixed with the modified blends. It can be seen that the corn plant heights planting in the soil mixed with the different blends EB irradiated to a dose of 50 kGy follow the order:
PLST/PV A/CS > PLST/PVA/AG > PLST/PVA

In addition, in Figure 16, the increase in chitosan (CS) ratio from 5% to 15% in the PLST/PVA blend improved the corn plant height from 50 to 60 cm. In the presence of magnesium.

Figure 17 shows the effect of PLST/PVA (85/15%) blends with CS or AG after loading with magnesium and EB irradiated to a dose of 50 kGy. It can be seen that when these blends were modified with Mg$^{2+}$, plant growth was greatly improved compared with those do not contain (Mg$^{2+}$). This improvement in corn plant growth using these blends may be due to the following effects:

1. These polymers improve the soil water holding capacity and water use efficiency.
2. Presence of NH$_2$ in chitosan improves the N$_2$ component in the soil.
3. The presence of chitosan and alginate in the modified blends will eventually acts as antimicrobial and antifungal and thus improves property of the soil.$^2$
4. As a result of electron beam irradiation, highly hydrophilic semi-interpenetrating network hydrogel was formed in which the network containing crosslinked PVA and the starch, forming hydrogen bonding, is included. This kind of structure will hold Mg$^{2+}$ ions and enhance the release in the soil as shown in scheme 1.
5. The biodegradability of the blends due to the presence of natural polymers had no harmful effects on the plant or the soil.

In a previous report, Influence of degradation of chitosan by gamma radiation on growth enhancement of corn planting was investigated.$^{26}$ The results showed that irradiated and unirradiated chitosan at concentrations ranging from 20, 50, and 100 ppm were effective for the growth promotion of corn plant, such as plant height, number of ear and ear size, in comparison with the control (untreated chitosan). It was found that the height of the corn plant after 57 days and treated with 20 ppm of unirradiated and irradiated chitosan was 60 and 65 cm, respectively. Comparable
results were found in the present work, in which the average height of corn plant was 90 cm after 45 days for the soil treated with EB irradiated PLST/PVA/CS blends, and EB irradiated PLST/PVA/AG blends in the presence of magnesium ions.

**Conclusion**

The present work was undertaken to apply electron beam irradiated natural blends based on plasticized starch (PLST), chitosan (CS) and alginate (AG) in the field of agriculture particularly in
improving the planting of corn plant. These natural blends have interesting properties such as non-toxicity, biocompatibility and biodegradability. Poly(vinyl alcohol) as radiation crosslinkable polymer was used to form bonding between the components of the blends through crosslinking reactions and thus the blend do not dissolve when were mixed with the planting soil. The results indicated the prepared modified blends were successfully improved the Rheological properties. In addition, the modified blends improved the corn planting, in which the height from 29 for unirradiated PLST/PVA blends to 40 cm after irradiation, from 40 cm to 50 and 54 cm after blending with AG and CS, respectively. The corn planting was greatly improved after using magnesium ions to reach 90 cm in the case of PLST/PVA/CS and PLST/PVA/AG blends.

Declaration of Conflicting Interests
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