

PREPARATION AND PROPERTY ANALYSIS OF BIODEGRADABLE PACKAGING FILM FROM ALGINATE, STARCH AND CITRIC ACID

NAZIA RAHMAN*, NIRMAL CHANDRA DAFADER, PARVIN BANU

*Nuclear and Radiation Chemistry Division, Institute of Nuclear Science and Technology,
Atomic Energy Research Establishment, Savar, Dhaka-1349, Bangladesh*

**Corresponding author: naziabaec@gmail.com*

ABSTRACT

In the present study alginate-starch blend films (thickness 0.08 mm) of different composition were prepared by casting and their mechanical properties were studied. Highest tensile strength was obtained for alginate: starch = 4: 1 of 70 MPa. To impart antimicrobial property to the alginate-starch films, citric acid of different composition was used and CaCl_2 treatment of this film was performed to improve the stability of the films in water. Then the films were further modified with monomer, methylacrylate (MA) and gamma radiation. The blend films were soaked in different formulations of methylacrylate (MA), in methanol and then irradiated by gamma radiation. Mechanical properties of the modified films such as tensile strength and elongation at break were studied. Thermal properties of films were characterized by dynamic mechanical analysis (DMA). The structural and morphological features of films were investigated using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

Keywords: biodegradable film; starch; alginate; citric acid; gamma radiation

INTRODUCTION

Introduction of biodegradable materials for packaging purpose instead of the common trend of petroleum based synthetic polymers has been encouraged by the claims of environmental protection. Synthetic polymers are widely used due to their excellent mechanical and thermal properties as well as their cost effectiveness. However, being non-biodegradable, these are a threat to environment. Hence, it is essential to develop biodegradable alternative packaging materials. Biodegradable films are usually fabricated from elements collected from natural sources. The production of biodegradable films from natural polymers has received much attention due to the excellent biodegradability, biocompatibility and edibility of the films. However, the major drawbacks of these films include poor mechanical properties and strong hydrophilic nature. That is why, multitude of studies are in progress to overcome these limitations to approach physicochemical quality similar to those of petrochemical properties [1-5].

In the present study alginate and starch has been used as the base material to prepare biodegradable film. Alginate is the water-soluble salt of alginic acid. It is distributed widely in the cell walls of brown algae [6-7]. The non-toxic polysaccharide, alginate consists of β -(1-4)-linked D-mannuronic acid (M) and α -(1-4) linked L-guluronic acid (G). Three types of glycosidic linkages exist in the block structures: diequatorial M-M, diaxial G-G and diequatorial-axial MG [8-10]. Alginate has unique colloidal and gel-forming properties that make it useful in preparing films or as a coating component [11-12]. Another useful and unique property of alginate is its ability to react with polyvalent metal cations, such as calcium ions in aqueous media, to form strong gels and insoluble polymers [13-16].

Starches are renewable resources, widely available and inexpensive. That is why they are widely used as a raw material to prepare biodegradable films [17-18]. Starch is a major food component and a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds [19]. It consists primarily of linear and branched chains of glucose molecules, namely amylose and amylopectin. Amylose is the linear fraction of starch and it is responsible for the development of coherent, relatively strong and free-standing films [20]. In contrast, the branched structure amylopectin generally leads to films that are brittle and reduced strength.

In this study citric acid was used to impart antimicrobial property of the alginate-starch films. Citric acid is a weak organic tri-basic acid. It occurs naturally in citrus fruits. Citric acid is known to have antimicrobial property and can improve the shelf life of food when used as food packaging [21]. The alginate-starch-citric acid films were treated with CaCl_2 to reduce the water solubility of the films. It is reported that CaCl_2 treatment can reduce the water solubility of alginate-starch film [22].

To improve the mechanical properties of natural polymer films various routes are followed. Such a route to accomplish the objective is graft copolymerization using electromagnetic radiation such as gamma ray, ultraviolet light and free radical initiators. Graft copolymerization of itaconic acid (IA) on sodium alginate (NaAlg) was performed in aqueous solution using benzoyl peroxide (BPO) as the initiator [23]. Preparation of gamma radiation grafted sodium alginate (SA)/polyethylene oxide (PEO) blend films using methacrylate monomer is reported [24]. Graft polymerization of methylacrylate onto granular starch was investigated [25]. Superabsorbent polymers were prepared from cassava starch-graft-poly(acrylamide) [26]. In the present study, grafting with acrylic monomer (methylacrylate) is carried out using γ radiation to improve the properties of alginate/starch based film. The use of γ radiation offers many advantages like continuous operation, minimum time requirement, less atmospheric pollution, design flexibility through process control [27].

In the present research work, alginate-starch blend films of different composition were prepared by casting and their mechanical properties were studied. To impart antimicrobial property to the alginate-starch films, citric acid of different composition were used. CaCl_2 treatment of the films was performed to improve the stability of the films in water. Then the films were further modified with methylacrylate (MA) monomer using gamma radiation. Mechanical properties of the modified films such as tensile strength and elongation at break were studied. Thermal properties of the films were characterized by DMA. The structural and morphological features of films were investigated using FTIR and SEM.

EXPERIMENTAL

Materials

Alginate and potato starch was purchased from Sigma Aldrich (Iceland), Citric acid and CaCl_2 was supplied by BDH chemicals (England). Methylacrylate (MA) was procured from Fluka Chemika (Switzerland).

Preparation of alginate-starch-citric acid films

A 4% w/v solution of alginate was prepared in distilled water by stirring with a glass rod for one hour. A 2% w/v solution of potato starch was prepared in distilled water by stirring with a glass rod in a water bath at 60°C for one hour. Then alginate-starch blends of different compositions, were prepared by mixing alginate and starch solution with magnetic stirrer

until homogeneous mixture obtained. Alginate-starch films (0.08 mm thick) were prepared from alginate-starch solution by casting and dried in an oven at 50°C. To impart antimicrobial property to alginate-starch films, citric acid was added to alginate-starch solution in different composition.

CaCl₂ treatment of alginate-starch-citric acid films

The alginate-starch-citric acid films were treated with 2% CaCl₂ in water for 2 min and then dried in an oven at 60°C for 30 min.

Modification of alginate-starch-citric acid film with MA using radiation

The alginate-starch-citric acid films after CaCl₂ treatment were further modified using MA and gamma radiation (10 - 40 kGy) from ⁶⁰Co. The blend films were cut into 60 x 10 mm² size and soaked in four different formulations of MA (M-1, M-2, M-3 and M-4) in methanol as shown in Table 1. The films were then sealed in polyethylene bag and irradiated by gamma radiation. Soaking time was varied from 5 - 20 min and radiation dose was varied from 10 - 40 kGy.

Table 1: Composition of different monomer formulations (M-1, M-2, M-3 and M-4) (w/w)

Formulations	Methanol (%)	MA (%)
M-1	95	5
M-2	90	10
M-3	85	15
M-4	80	20

Tensile Properties

Tensile properties of the films were measured using Universal Testing Machine (Testometric, model M 500-100CT, UK). The crosshead speed and gauge length were 2 mm/min and 20 mm respectively with load range 250 N throughout the experiment.

Polymer loading

The polymer loading (PL) of the films was determined on the basis of weight gain by the film after the MA treatment process with radiation (followed by washing with methanol to remove homo-polymers). The PL was determined by the following equation:

$$PL (\%) = (W_t - W_0) / (W_0 \times 100)$$

where, W_t is the weight of the MA treated film after irradiation (followed by washing with methanol) and W_0 is the weight of the film before MA treatment. The weight was calculated on dry basis.

Water Uptake

Water uptake was measured by soaking the films in distilled water contained in a static beaker at 25°C for 4 h. The water uptake was calculated by the following equation:

$$\text{Water uptake (\%)} = (W_w - W_d) / (W_d \times 100)$$

where W_w is the weight of the wet film and W_d is the weight of the dry film.

Dynamic Mechanical Analysis

The thermal properties of films were studied from 27°C to 200°C at a rate of 4°C/min and an oscillating frequency of 1 Hz using Dynamic Mechanical Analyzer (DMA), Triton Technology TTDMA, UK.

Fourier Transform Infrared Spectroscopy (FTIR)

The alginate, alginate-starch-citric acid and irradiated alginate-starch-citric acid films were characterized by FTIR (ATR) spectrophotometer (8400S Shimadzu Japan) in the range 700-4000 cm⁻¹ (resolution 4 cm⁻¹, number of scans: 20 times).

Scanning Electron Microscopy (SEM)

The morphological study of the alginate, alginate-starch-citric acid and irradiated alginate-starch-citric acid films was done by using scanning electron microscopy (SEM) of Model JEOL 6400 at an accelerating voltage of 15 kV. The SEM specimens were sputter coated with platinum.

Storage of Lady's Finger (*Abelmoschus esculentus*)

Lady's finger of known weight were stored in alginate-starch-citric acid film for 7 days. The weight loss and physical appearance of the lady's finger with respect of control were compared. Weight loss was calculated as follows:

$$\text{Weight loss (\%)} = (W_1 - W_t) / (W_1 \times 100)$$

where W_1 is the initial weight of lady's finger and W_t is the weight of lady's finger at 't' time.

RESULTS AND DISCUSSION

Alginate and alginate-starch blend films with and without citric acid (0.08 mm thick) were prepared by casting. For all alginate-starch blend films without citric acid, the tensile strength was found higher than that of pure alginate film. This result may be due to entanglement/physical bonding obtained in polymer chains. Highest tensile strength was obtained for alginate: starch = 4: 1 (w/w) films. The tensile strength and elongation at break of the alginate: starch = 4: 1 (w/w) film was 70 MPa and 1.4 % respectively. To impart antimicrobial property to the alginate-starch films, citric acid was added to alginate-starch solution in different composition. The citric acid concentration was varied from 10 % to 50 % of total polymer (alginate + starch) weight. The tensile strength of alginate-starch blend film with citric acid was lower than that of pure alginate film and alginate-starch blend film without citric acid. This result can be explained as citric acid may act as a plasticizer. The addition of citric acid in alginate/starch blend reduces the intermolecular attraction between macromolecules and thus decreases tensile strength of blend film. It is reported that citric acid acts both as cross-linker and plasticizer [28]. The tensile strength of poly(vinyl alcohol)/starch blend increased at 5% citric acid and after this concentration of citric acid, a decreasing trend of tensile is found of poly(vinyl alcohol)/starch blend film. The tensile strength and elongation at break of alginate, alginate-starch films with and without citric acid are shown in Table 2. To get best antimicrobial effect, the films with 50% citric acid was selected for further processing.

To improve the stability in water, the alginate-starch-citric acid blend films were treated with CaCl₂. Alginate reacts with polyvalent metal in aqueous media and makes it insoluble [14, 29]. It was found that alginate and alginate-starch films dissolved within 1 minute. However, alginate-starch-citric acid remained stable up to 10 minutes. This result may be due to the interaction of carboxyl group of citric acid and hydroxyl group of polymer

chains. On the other hand, the film after CaCl_2 treatment became stable in distilled water up to 12 days (Table 3).

Table 2: The tensile properties of alginate and alginate-starch blend film.

Composition of film (w/w)			Tensile Strength (MPa) of film	Elongation at Break (%) of film
Alginate (php)*	Starch (php)*	Citric acid (php)*		
100	0	0	60	1.8
80	20	0	70	1.4
75	25	0	67	1.5
60	40	0	65	1.6
80	20	10	50	0.6
80	20	20	40	0.5
80	20	30	20	0.7
80	20	40	50	0.9
80	20	50	45	1.0

* Per hundred part of polymer (Alginate + Starch)

Table 3: Water stability of the alginate and alginate-starch blend films

Sample film	Solubility in water
Alginate	Soluble within 1 min
Alginate-starch	Soluble within 1 min
Alginate-starch-citric acid	Soluble within 10 min
Alginate-starch-citric acid (treated with CaCl_2)	Remained stable up to 12 days

Therefore the alginate/starch blend film was prepared from alginate/starch blend solution with 50 wt% citric acid of total polymer and treated with CaCl_2 for reducing solubility in water. However after CaCl_2 treatment the tensile strength of the film decreased to 16 MPa and the elongation at break reached to 5%. This result may be due to the fact that some of the calcium chloride molecules interact with carboxyl group of alginate and others interact with carboxyl group of citric acid. It is reported that calcium chloride reacts with carboxyl group of alginate and improved the tensile strength of sago starch/alginate blend film [22]. Then the obtained films were radiation modified using methacrylate. The blend films were soaked in different formulations of MA as monomer (5% - 20%) in methanol and then irradiated by gamma radiation. Soaking time was varied from 5-20 min and radiation dose was varied from 10-40 kGy. Monomer concentration, soaking time and gamma radiation dose were optimized on the basis of mechanical properties.

The alginate-starch-citric acid films treated with CaCl_2 were soaked in different formulations of MA as monomer (M1-M4) for 10 min. The films were then irradiated by gamma radiation at 30 kGy. After 24 hr of radiation, mechanical properties of modified films were determined. The tensile strength (TS) of radiation modified films as a function of monomer concentration is presented in Fig. 1. For 5% MA, TS value was found 17.3 MPa. TS values increased with increasing the percentage of MA in solution and reached the maximum value of 26.98 MPa for 10% MA (M2 formulation) which is 68% higher than the TS value of the film before irradiation. After 10% MA the TS values of the film decreased with increasing MA concentration and reached to 23 MPa for 20 % MA. At low monomer concentration, vinyl monomer like MA promotes monomer-polymer back bone reaction [30]. As monomer concentration increases, more MA may undergo polymerization and the TS increased. However, at higher MA concentration TS decreased due to the dominated

recombination process, thus creating homo-polymer rather than monomer-polymer back bone reaction [31-32]. To support this statement the MA treated irradiated blend films (prepared using 10 % MA and 20 % MA) were washed with methanol and dried. The blend film prepared using 10 % MA showed 0 % weight loss whereas film prepared using 20 % MA showed 5 % weight loss. These results indicate that homo-polymers were formed during radiation treatment with 20 % MA concentration that washed out in methanol.

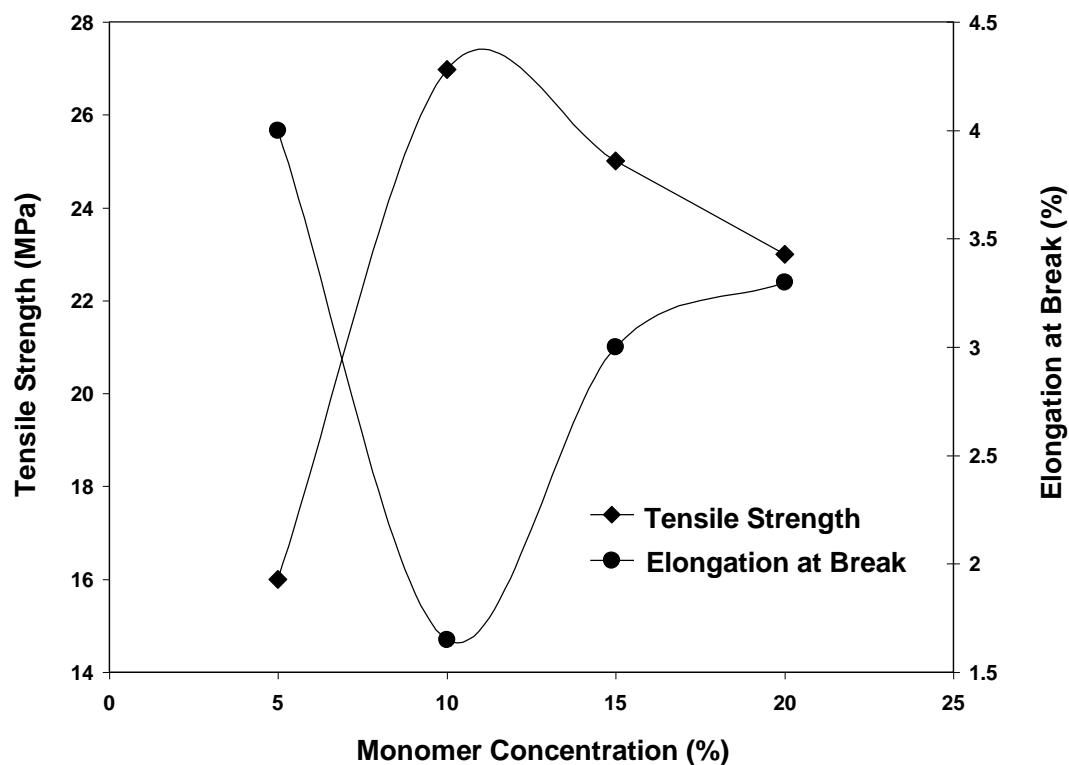


Fig. 1 Change of tensile strength and elongation at break with change of monomer concentration.

Elongation at break (Eb) of the irradiated films was studied as a function of monomer concentrations and the results are presented in Fig. 1. It was observed that for all monomer concentration Eb found after radiation treatment was lower than the Eb of the film before irradiation. For 5% MA, Eb was found to be 4%. Eb decreased with increase in the percentage of MA and reached the minimum of 1.65% for 10% MA. After 10% MA the Eb values of the film increased with increasing MA concentration and reached to 3.3 % for 20% MA. After MA treatment using gamma radiation the rigidity of the film increased causing decrease of Eb.

On having the highest TS for 10% MA (M2 formulation), the TS and Eb values of irradiated films were studied as a function of radiation dose for 10% MA at 10 min soaking time. The TS values of the irradiated films as a function of radiation dose are presented in Fig. 2. For 10 kGy TS was found 18.73 MPa. TS increased with increase in the radiation dose and reached the maximum of 26.98 MPa for 30 kGy radiation dose. After the 30kGy radiation dose TS values of the film decreased with increasing radiation dose and reached to 23 MPa for 40 kGy radiation dose. It is expected that with the increase of radiation dose some active sites were generated in polymer backbone and MA. These active sites may react with each other and can form copolymer. As a result, the TS increased. Nevertheless, at higher radiation dose, homo-polymer formation suppresses reaction between polymer and MA. This

phenomenon is quite common for natural biopolymers as reported earlier by other researchers [33-34]. Thus, at high radiation dose, the film became brittle and the TS decreased.

Elongation at break (Eb) of the irradiated films was studied as a function of radiation dose and the results are presented in Fig. 2. It was observed that for Eb of film after radiation treatment was lower than the Eb of the film before irradiation. For 10kGy Eb was found to be 3.35 %. Eb decreased with increase in the radiation dose and reached the minimum of 1.65 % for 30 kGy. After 30 kGy Eb values of the film increased with increasing radiation dose and reached to 2.7 % for 40 kGy.

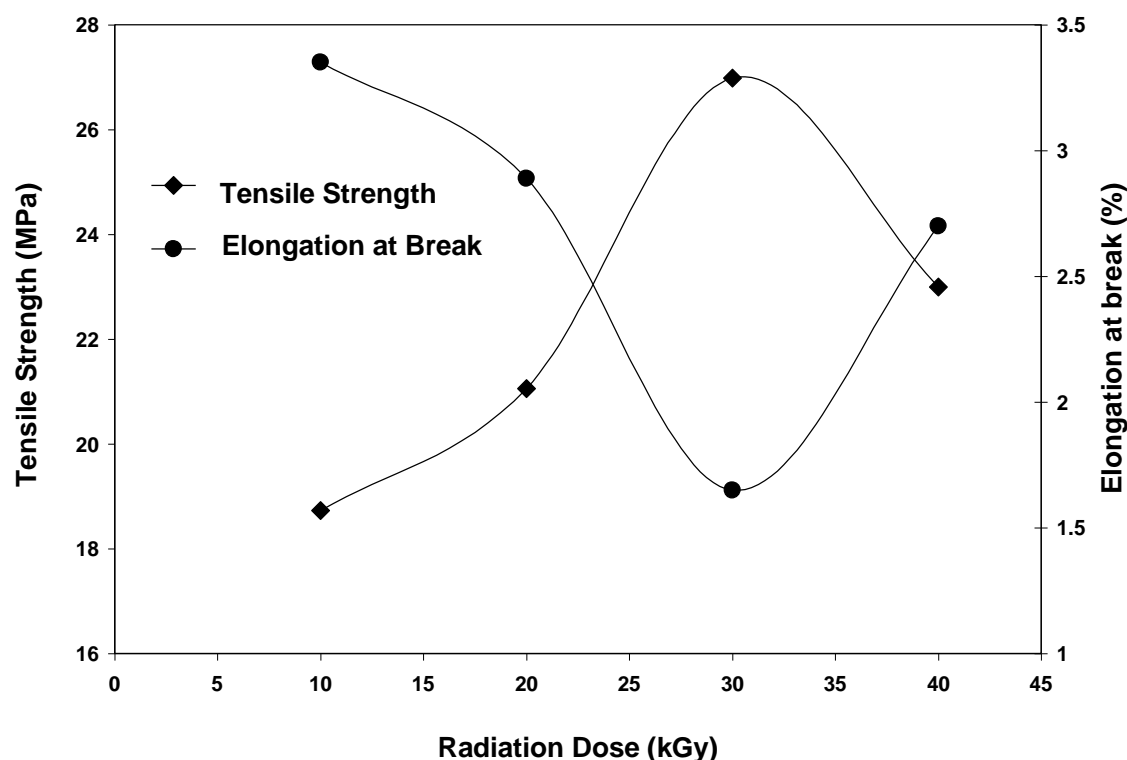


Fig. 2 Change of tensile strength and elongation at break with change of radiation dose.

On having the highest TS for M2 formulation and 30kGy gamma radiation dose, the blended films were soaked in M2 for different soaking times (5, 10, 15 and 20 min) and then irradiated at 30 kGy radiation. After 24 h of radiation, TS and Eb were investigated. The changes of TS of alginate-starch-citric acid films as a function of soaking time are shown in Fig. 3. From Fig. 3, it was observed that TS was found 17.3 MPa for 5 min soaking time. TS increased with increase in soaking time and reached the maximum of 26.98 MPa for 10 min soaking time. Increase of soaking time caused more diffusion of monomer into the sites of reaction and thus increased the possibility of formation of copolymer by reaction between monomer and polymer [35]. Thus with increase of soaking time more MA came in contact with alginate to form cross linked network polymer and the TS of the films increased. However, with further increase of soaking time the film became twisted, shrank and TS decreased.

Elongation at break of the irradiated films was studied as a function of soaking time and the results are presented in Fig. 3. It was observed that for all soaking time Eb found after radiation treatment was lower than the Eb of the film before irradiation. For 5 min soaking time Eb was found be 3.8 %. Eb decreased with increase in the soaking time and reached the minimum of 1.65 % for 10 min soaking time. After 10 min Eb values of the alginate-starch-

citric acid film increased with increasing soaking time and reached to 3 % for 20 min. After MA treatment using gamma radiation the rigidity of the film increased causing decrease of Eb.

Thus the best performance was observed for the alginate-starch-citric acid film soaked in 10 % monomer solution for 10 min soaking time and irradiated by 30-kGy radiation dose. The TS and Eb found under this condition was 26.98 MPa and 1.65 % respectively.

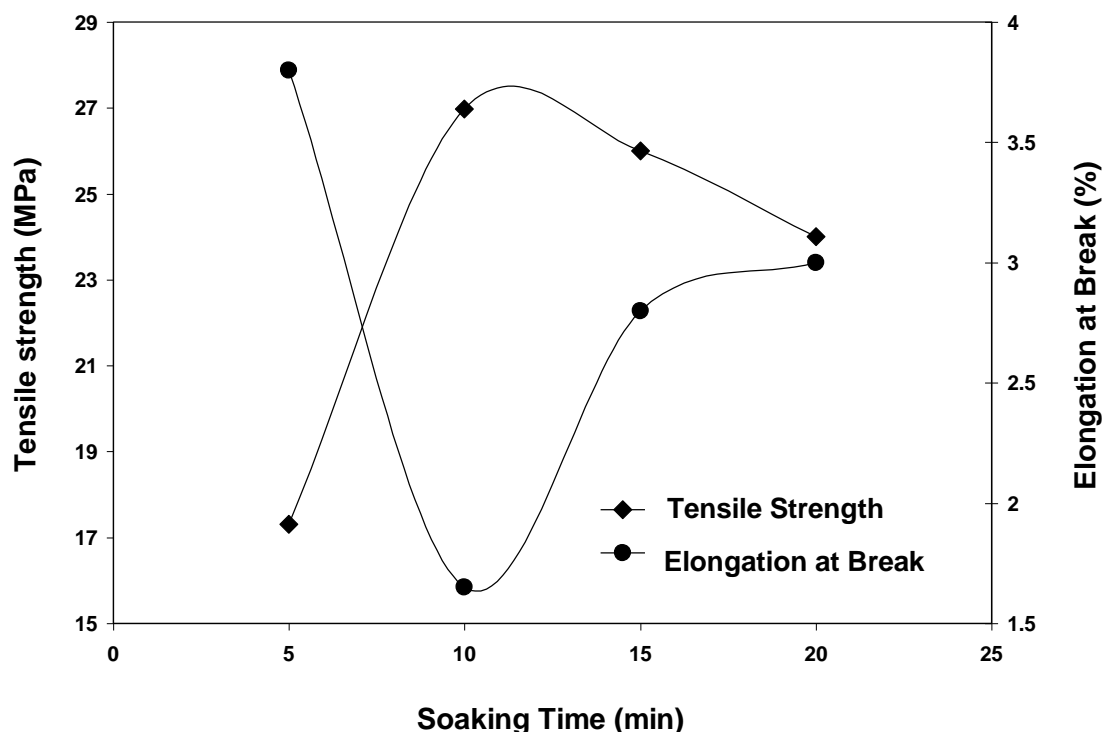


Fig. 3 Change of tensile strength and elongation at break with change of soaking time.

Polymer Loading

Polymer loading (PL) values of the irradiated films were studied and presented as a function of radiation dose for 10 % MA at 10 min soaking time in Table 3. For 10 kGy, PL was 13 %. PL increased with increase in the radiation dose and reached the maximum of 25 % for 30 kGy radiation dose. After the 30 kGy radiation dose PL value of the blend film decreased with increasing radiation dose and reached to 22 % for 40 kGy radiation dose. The PL values obtained are in agreement with the mechanical properties.

Table 3: Polymer loading of the MA treated irradiated blend film at various radiation dose.

Radiation Dose (kGy)	Polymer loading (%)
10	13
20	18
30	25
40	22

Water Uptake

Water Uptake values of the irradiated films were studied to estimate quantitatively the formation of crosslink. The results as a function of radiation dose for 10 % MA at 10 min

soaking time are shown in Table 4. For 10 kGy, water uptake was 65 %. Water Uptake decreased with increase in the radiation dose due to formation of crosslink and reached the minimum of 50 % for 30 kGy radiation dose. After the 30 kGy radiation dose water uptake values of the blend film increased with increasing radiation dose and reached to 55 % for 40 kGy radiation dose. The water uptake values obtained are in accordance with the mechanical properties.

Table 4: Water Uptake of the MA treated irradiated blend film at various radiation dose.

Radiation Dose (kGy)	Water Uptake (%)
10	65
20	58
30	50
40	55

Dynamic Mechanical Properties

For the determination of the dynamic mechanical properties of polymeric materials, the glass transition phenomena are important factors. DMA was used to investigate the phase relaxation behavior of alginate films in this work. Fig. 4 shows the change in the storage modulus of alginate films. In all cases modulus at first increases, reaches a maximum and then decreases. For pure alginate (Al), modulus increases up to 90 °C and then storage modulus started to decrease. This transition, called the α -transition, (T_α), around 90 to 110 °C, is defined as glassy region. After the sharp drop of the storage modulus in the glass transition region, the behavior of alginate film moves to the leathery state plateau region caused by the micro-Brownian motion of non-crystalline region between 110 to 190 °C. For alginate-starch-citric acid (Al-St-Ci) film the glass transition region started around 174 °C. For MA treated irradiated alginate-starch-citric acid (Al-St-Ci-MA-irradiated) film the glass transition region occurred between 103 and 173°C.

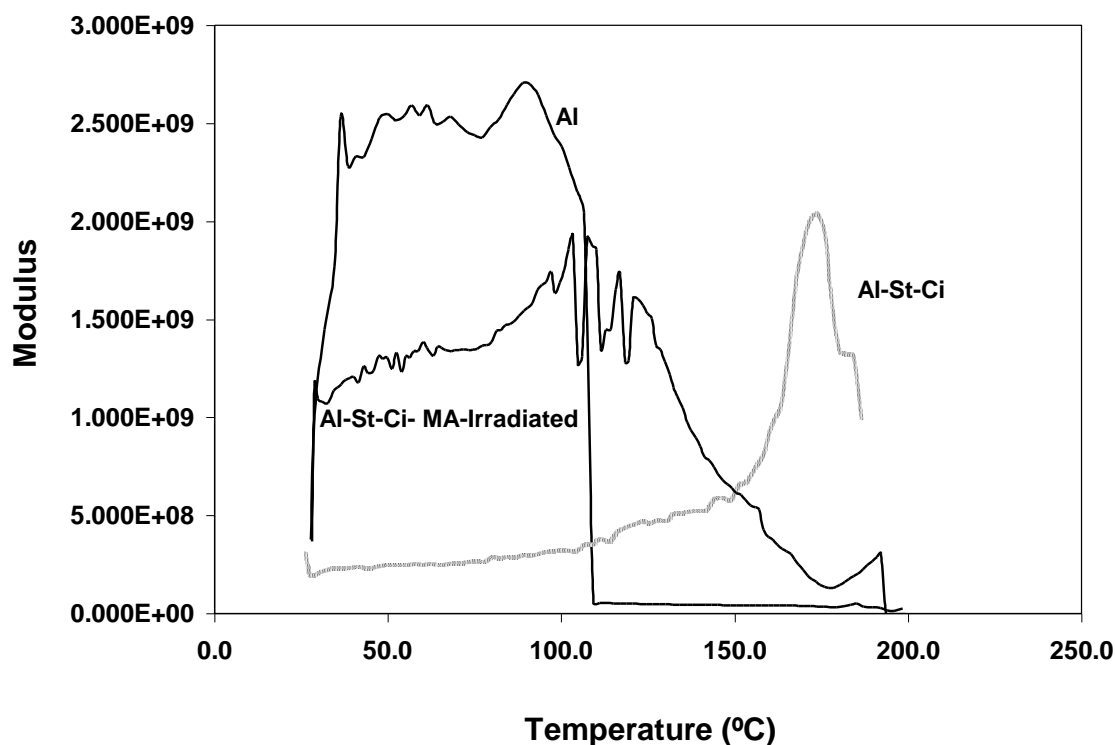


Fig. 4 Dynamic Modulus as a function of temperature for different alginate films.

FTIR analysis of alginate films

The spectrum of alginate film (Fig. 5(a)) showed absorption bands around 1597 cm^{-1} , 1408 cm^{-1} , and 1298 cm^{-1} that are attributed to stretching vibrations of asymmetric and symmetric bands of carboxylate anions, respectively. The peak appeared at 3271 cm^{-1} corresponds to stretching vibrations of hydroxyl groups. Peak at 1074 cm^{-1} is characteristic of a C-O-H bond. The spectrum of alginate-starch-citric acid film (Fig. 5(b)) showed all the peaks that appeared in the spectrum of alginate film with little shift. Two new peaks appeared at 2981 cm^{-1} and 1730 cm^{-1} can be assigned to C-H and C=O bond stretching. The spectrum of MA treated irradiated alginate-starch-citric acid film (Fig. 5(c)) showed similar peaks that appeared in the spectrum of alginate-starch-citric acid film with little shift. The shift of peak for hydroxyl group from 3284 cm^{-1} to 3304 cm^{-1} and the broadening of hydroxyl group peak indicates that some -OH groups might have interacted with MA monomer during irradiation.

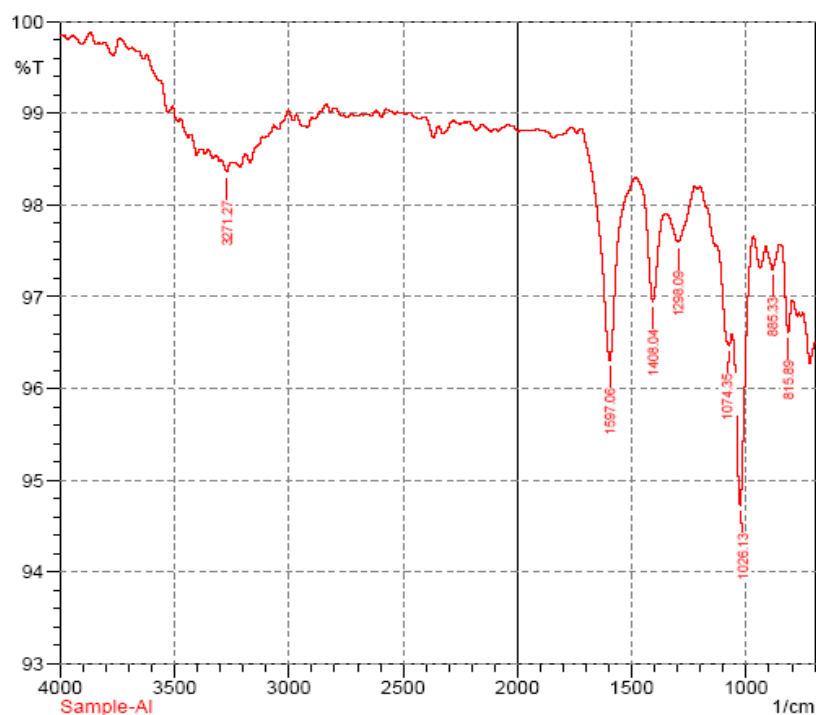


Fig. 5(a) FTIR spectrum of alginate film

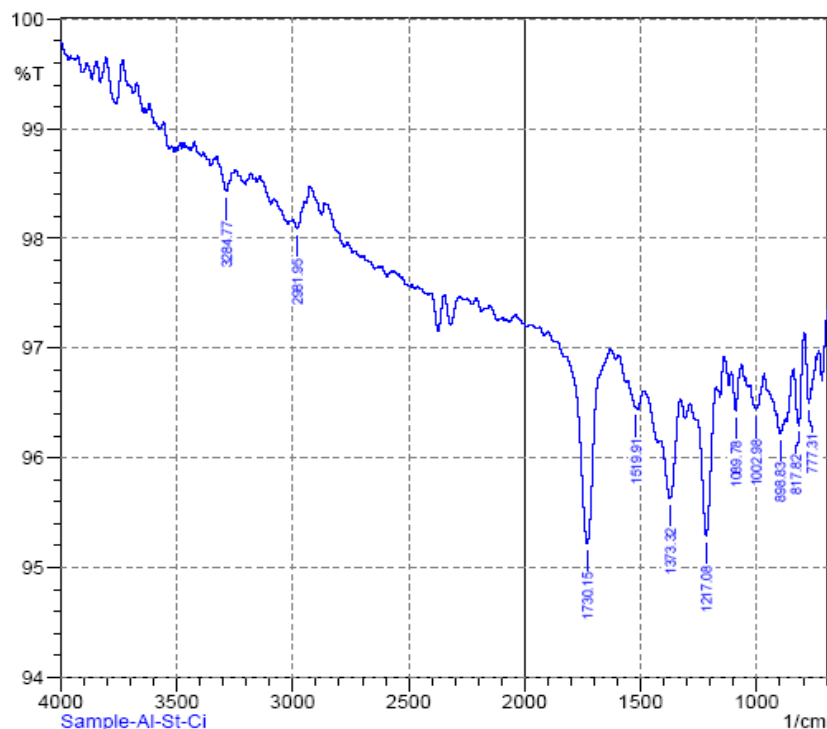


Fig. 5(b) FTIR spectrum of alginate-starch-citric acid film

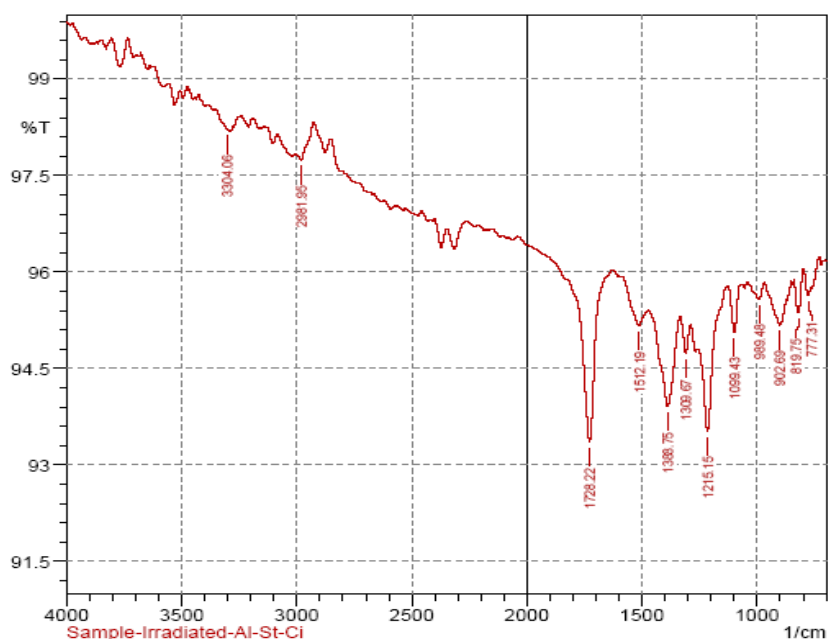


Fig. 5(c) FTIR spectrum of MA treated irradiated alginate-starch-citric acid film

SEM Analysis of alginate films

The surface morphology of alginate, alginate-starch-citric acid and alginate-starch-citric acid radiation modified with MA are shown in Fig. 6(a), Fig. 6(b), Fig. 6(c). The surface of alginate film was smooth while the SEM image of alginate-starch-citric acid blend film showed a rough surface. Again alginate-starch-citric acid film after radiation modification with MA showed clear change of surface morphology due to interaction of MA with the blend film.

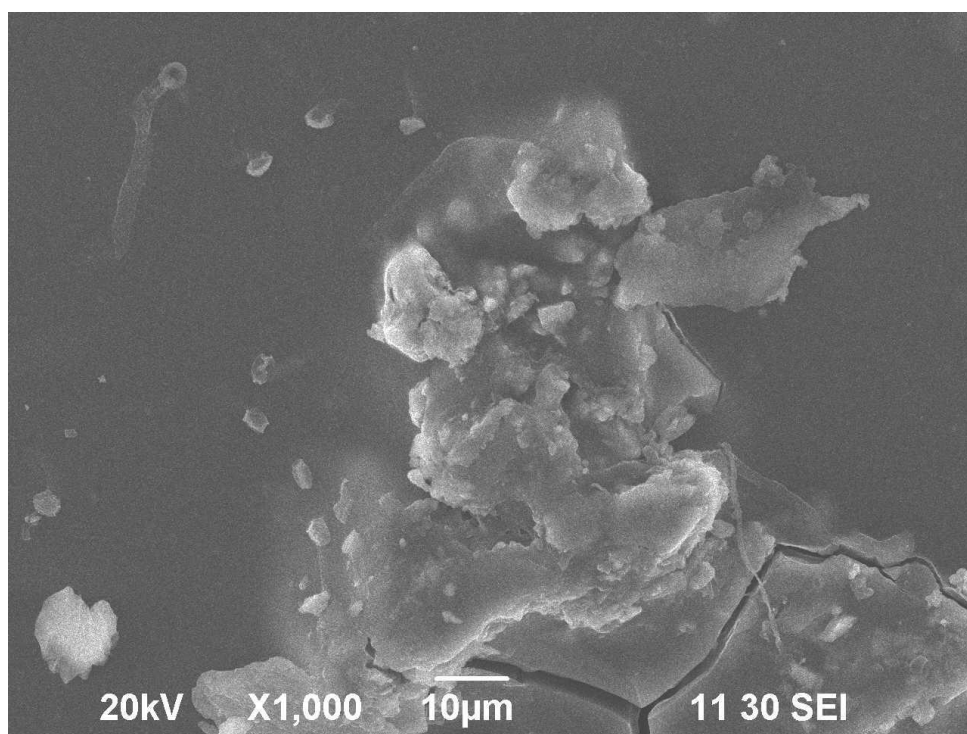


Fig. 6(a) SEM image of alginate film



Fig. 6(b) SEM image of alginate-starch-citric acid film

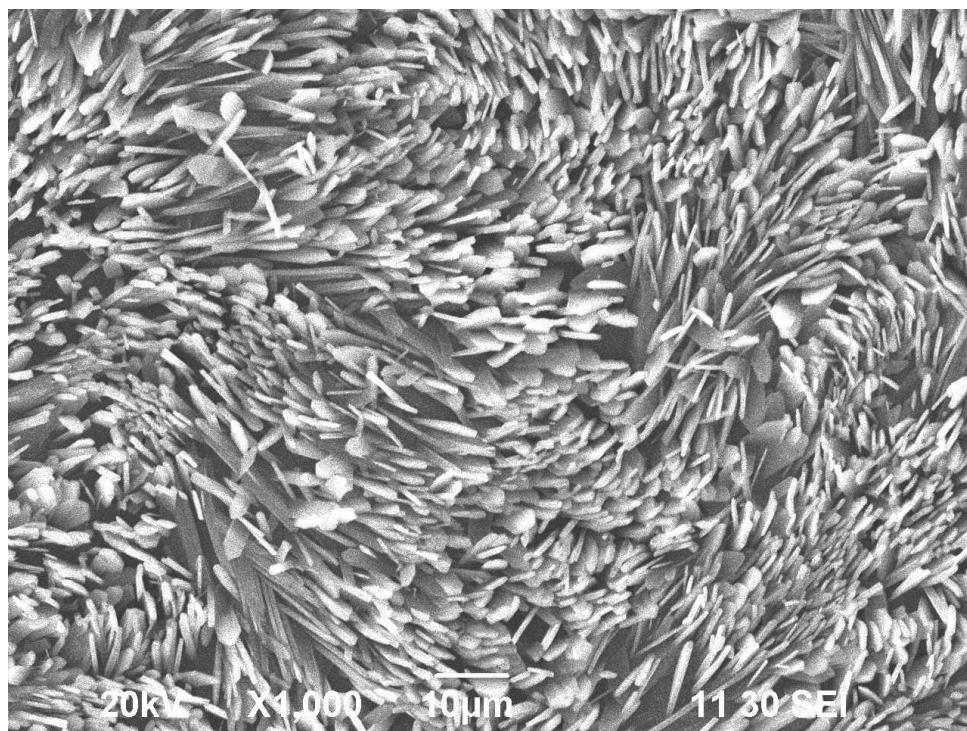


Fig. 6(c) SEM image of MA treated irradiated alginate-starch-citric acid film

Storage of Lady's Finger (*Abelmoschus esculentus*) in alginate-starch-citric acid film

Lady's finger (*Abelmoschus esculentus*) of known weight was stored in alginate-starch-citric acid film (thickness 0.08 mm) for 7 days. The physical appearance of the lady's finger stored in biodegradable film is compared with control in Fig. 7. The weight loss of the lady's finger stored in biodegradable film is compared with control in Table 3. It is observed that the lady's finger stored in biodegradable film showed less weight loss than control indicating that the biodegradable film can improve the shelf life of lady's finger.

Table 3: The weight loss of the lady's finger stored in biodegradable film is compared with control

Lady's Finger Storage	Weight loss (%)				
	1 day	2 days	3 days	4 days	7 days
In air	35	44	54	62	78
In alginate-starch-citric film	24	33	44	53	67



Fig. 7 (a) After 0 day in alginate-starch-citric acid film, (b) After 7 day in alginate-starch-citric acid film (c) Control after 0 day (d) Control after 7 day

CONCLUSION

Alginate-starch blend films (thickness 0.08 mm) of different compositions were prepared by casting and their mechanical properties were studied. Good mechanical properties were obtained for alginate: starch = 4: 1 (w/w) films. The tensile strength and elongation at break of the alginate: starch = 4: 1 (w/w) film was 70 MPa and 1.4 % respectively. To impart antimicrobial property to alginate-starch films, citric acid was added to alginate-starch solution in different composition. The films were treated with CaCl_2 . Water stability of the film improved significantly after CaCl_2 treatment; however the TS decreased to 16 MPa. Therefore the films were further modified with monomer methylacrylate (MA) using gamma radiation. The best performance was observed for the alginate-starch-citric acid film soaked in 10 % monomer solution for 10 min soaking time and irradiated by 30-kGy radiation dose. The TS and Eb found under this condition was 26.98 MPa and 1.65 % respectively. Thermal properties of the films were studied by dynamic mechanical analysis (DMA). The films were also investigated using FTIR and SEM. Storage of lady's finger in biodegradable film showed less weight loss than control indicating that the biodegradable film can improve the shelf life of lady's finger.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge for financial support from IAEA under the Research Contract No. 17639. Authors also would like to thank the Gamma Source Division of

Institute of Food and Radiation Biology, Atomic Energy Research Establishment for providing us the opportunity to use the irradiation facility.

REFERENCES

1. Salmieri S, Lacroix M (2006) Physicochemical properties of alginate/polycaprolactone-based films containing essential oils. *J Agric Food Chem* 54:10205-10214.
2. Rooney M L (1995) Overview of active food packaging. Rooney Chapman and Hall, London.
3. Suppakul P, Miltz J, Sonneveld K, Bigger SW (2003) Active packaging technologies with an emphasis on antimicrobial packaging and its applications. *J Food Sci* 68:408–420.
4. Tien CL, Letendre M, Ispas SP, Mateescu MA, Delmas PG, Yu IL, Lacroix M (2000) Development of biodegradable films from whey proteins by cross-linking and entrapment in cellulose. *J Agric Food Chem* 48:5566–5575.
5. Ciesla K, Salmieri S, Lacroix M (2006) γ -Irradiation influence on the structure and properties of calcium caseinate–whey protein isolate based films. Part 2. Influence of polysaccharide addition and radiation treatment on the structure and functional properties of films. *J Agric Food Chem* 54:8899–8908.
6. Rubio MR, Ghaly ES (1994) In vitro release of acetaminophen from sodium alginate controlled release pellets. *Drug Dev Ind Pharm* 20: 1239-1251.
7. Al-Musa S, Abu Fara D, Badwan AA (1999) Evaluation of parameters involved in preparation and release of drug loaded in crosslinked matrices of alginate. *J Control Release*, 57: 223-232.
8. Yotsuyanagi T, Yoshioka, I, Segi N, Ikeda K (1991) Acid-induced and calcium induced gelation of alginic acid: Bead formation and pH dependent swelling. *Chem Pharm Bull* 39: 1072-1074.
9. Donati I, Holtan S, Mørch YA, Borgogna M, Dentini M (2005) New hypothesis on the role of alternating sequences in calcium–alginate gels. *Biomacromolecules* 6: 1031-1040.
10. Dong Z, Wang Q, Du Y (2006) Alginate/gelatin blend films and their properties for drug controlled release. *J Membr Sci* 280: 37-44.
11. King AH (1982) In: M. Glicksman (ed) *Brown seaweed extracts (alginates)*, FL: CRC Press, Boca Raton.
12. Rhim JW (2004) Physical and mechanical properties of water resistant sodium alginate films. *Lebensm Wiss Technol* 37: 323-330.
13. Grant GT, Morris ER, Rees DA, Smith PJC (1973) Biological interactions between polysaccharides and divalent cations: The egg-box model. *FEBS Letters* 32: 195-198.
14. Braccini I, Pérez S (2001) Molecular basis of Ca^{2+} -induced gelation in alginates and pectins: the eggbox model revisited. *Biomacromolecules* 2: 1089-1096.
15. Fang Y, Al-Assaf S, Phillips GO, Nishinari K, Funami T, Williams PA (2008) Binding behavior of calcium to polyuronates: Comparison of pectin with alginate. *Carbohydr Polym* 72: 334-341.
16. Olivas GI, Barbosa-Cánovas GV (2008) Alginatecalcium films: Water vapor permeability and mechanical properties as affected by plasticizer and relative humidity. *LWT Food Sci Technol* 41: 359-366.
17. Mali S, Grossmann MVE (2003) Effects of yam starch films on storability and quality of fresh strawberries (*Fragaria ananassa*). *J Agric Food Chem* 51: 7005-7011.

18. Famá L, Rojas AM, Goyanes S, Gerschenson L (2005) Mechanical properties of tapioca-starch edible films containing sorbates. *LWT Food Sci Technol* 38: 631-639.
19. Zhou YG, Wang, LJ, Li D, Yan PY, Li Y, Shi J, Chen XD, Mao JH (2009) Effect of sucrose on dynamic mechanical characteristics of maize and potato starch films. *Carbohydr Polym* 76: 239-243.
20. Rindlav-Westling A, Stading M, Hermansson AM, Gatenholm P (1998) Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydr Polym* 36: 217-224.
21. In, YW, Kim JJ, Kim HJ, Oh SW (2013) Antimicrobial Activities of Acetic Acid, Citric Acid and Lactic Acid against *Shigella* Species. *J Food Safety* 33: 79-85.
22. Fazilah A, Maizura M, Abd Karim A, Bhupinder K, Rajeev B, Uthumporn U, Chew SH (2011) Physical and mechanical properties of sago starch – alginate films incorporated with calcium chloride, *Int Food Res J* 18: 1027-1033.
23. Işıklan N, Kurşun M, İnal M (2010) Graft copolymerization of itaconic acid onto sodium alginate using benzoyl peroxide, *Carbohydr Polym* 79: 665–672.
24. Dafader NC, Rahman W, Sumi SA (2017) Breakthrough in the preparation of irradiated sodium alginate/polyethylene oxide blend films using methacrylate monomer, *Int J Polym Anal Ch.* 22: 152-159.
25. Trimnell D, Fanta GF, Salch JH (1996) Graft polymerization of methyl acrylate onto granular starch: Comparison of the $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ and ceric initiating systems, *J appl Polym Sci* 60: 285-292.
26. Parvathy PC, Jyothi AN (2012) Synthesis, characterization and swelling behaviour of superabsorbent polymers from cassava starch-graft-poly(acrylamide). *Starch*, 64: 207-218.
27. Ghosal S, Khan MA, Noor FG, Khan RA (2009) Gamma radiation induced biodegradable shellac films treated by acrylic monomer and ethylene glycol. *J Macromol Sci Part A:Pure appl Chem.* 46: 975-982.
28. Rui S, Jingliang B, Zizheng Z, Aichen Z, Dafu C, Xinhua Z, Liquan Z, Wei T (2008) The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydr Polym* 74: 763–770.
29. Grant G T, Morris ER, Rees DA, Smith PJC (1973) Biological interactions between polysaccharides and divalent cations: The egg-box model. *FEBS Letters* 32: 195-198.
30. Khan M A, Rahman MA, Khan RA, Rahman N, Islam JMM, Alam R, Mondal MIH (2010) Preparation and characterization of the mechanical properties of the photocured chitosan/starch Blend Film. *Polym Plast Technol Eng* 49: 748–756.
31. Alam R, Khan MA, Khan RA, Ghoshal S, Mondal MIH (2008) Study on the physico-mechanical properties of photo-cured chitosan films with oligomer and acrylate monomer. *J Polym Environ* 16: 213–219.
32. Nunthanid J, Puttipipatkachorn S, Yamamoto K, Peck GE (2001) Physical properties and molecular behavior of chitosan films. *Drug Dev Ind Pharm* 27: 143–157.
33. Khan MA, Khan RA, Noor FG, Rahman MM, Alam MN (2009) Studies on the mechanical properties of gelatin and its blends with vinyltrimethoxysilane: Effect of gamma radiation. *Polym Plast Technol Eng* 48: 813–818.
34. Ghoshal S, Khan MA, Noor FG, Khan RA (2009) Gamma radiation induced biodegradable shellac films treated by acrylic monomer and ethylene glycol. *J Macromol Sci Chem Part. A.* 46: 975–982.
35. Rahman N, Khan MA, Khan RA, Chowdhury TA (2011) Modification of Gelatin Films Using Trimethylolpropane Trimethacrylate (TMPTMA) by Photo-Curing, *Polym Plast Technol Eng* 50: 404–411.