

## MODIFICATION OF MECHANICAL AND THERMAL PROPERTIES OF CHITOSAN-PVA BLEND FILMS USING RADIATION TECHNIQUE

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### ABSTRACT

In this study casting method is used to prepare different composition of chitosan-PVA blend films (thickness 0.16 mm). Optimum composition (chitosan: PVA = 1: 4) of the blend film was selected based on mechanical properties. The tensile strength (TS) and elongation at break (Eb) of the film at this composition was 24 MPa and 20 % respectively. The chitosan-PVA films were modified with monomer, methyl methacrylate (MMA) using gamma radiation. Monomer concentration was varied from 1-7 %, soaking time was varied from 10-30 min and radiation dose was varied from 10 kGy-40 kGy. Mechanical properties of the modified films were investigated. The best performance was observed for the chitosan-PVA films soaked in 3% monomer solution for 20 min soaking time and irradiated by 30 kGy radiation dose. The TS and Eb found under this condition were 36 MPa and 34 % respectively. Water uptake of the films was studied. Thermal properties of films were characterized by thermo gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The molecular interaction and morphological features of the films were investigated using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

**Keywords:** chitosan; poly(vinyl alcohol); blend film; radiation modification.

### INTRODUCTION

Recent global ecological consciousness boosts the use of biodegradable materials instead of the dominant tendency of petroleum based synthetic polymers for packaging purpose. The production of biodegradable films from natural polymers has received much attention due to the excellent biodegradability, biocompatibility and edibility of the films [1-5]. Blending of synthetic and natural polymers is one of the beneficial ways to produce new material with desirable properties. Chitosan (Cs) is produced from chitin that is found in the exoskeleton of insects, shells of crustaceans or various fungi. Chitosan is a partially deacetylated form of chitin [6-10]. This chitin is the most abundant natural polymer next to cellulose [11]. Unlike chitin, chitosan is soluble in acid solutions. Chitin and chitosan have remarkable uses in the biomedical field due to their good biocompatibility, biodegradability, and capacity to form membranes, beads, fibers, scaffold and gels [12–15]. Chitosan prevents the growth of a wide variety of fungi, yeasts, and bacteria. Poly(vinyl alcohol) (PVA) is a biodegradable, biocompatible, non-carcinogenic synthetic polymer. Because of its good film forming and highly hydrophilic property with outstanding chemical stability it was blended with different synthetic and natural polymers. It is useful in many applications such as controlled drug delivery systems, film formation, packaging etc. Because of

the promising properties of chitosan and PVA, fabrication of blend films from chitosan and PVA and their further modification can be a route to produce packaging materials with desirable properties.

Graft copolymerization using electromagnetic radiation is an important way to improve the properties of polymer films. Grafting is the method by which monomers with desirable properties are covalently bonded to the backbone polymer chain. Chitosan was grafted using acrylic monomers, ethylene glycol and ethylene glycol dimethacrylate and reported to achieve higher mechanical properties keeping its inherent biodegradable properties [16-18]. Poly(methyl methacrylate) (PMMA) is a thermoplastic polyester possessing outstanding properties such as light weight, low cost, biocompatibility etc [19]. Due to the excellent biocompatibility, methyl methacrylate (MMA) was chosen for graft co-polymerization.

In the present research work, chitosan-PVA blend-films of different composition were prepared and their mechanical properties were studied. Chitosan-PVA films were modified with monomer methyl methacrylate (MMA) using gamma radiation. Monomer concentration was varied from 1-7 %, soaking time was varied from 10-30 min and radiation dose was varied from 10-40kGy. Mechanical properties of the modified films were studied. Thermal properties of the films were analyzed by TGA and DMA. SEM and FTIR were used to study the morphological and structural features of the blend film, respectively. Water uptake of the films was also studied.

## EXPERIMENTAL

### Materials

Chitosan was purchased from Sigma Aldrich (Iceland). Poly(vinyl alcohol), acetic acid, MMA and methanol were supplied by Merck (Germany).

### Preparation of Chitosan-PVAFilms

A 1% w/v solution of chitosan was prepared in 2 % aqueous acetic acid at room temperature with stirring. PVA was dissolved in hot distilled water to prepare a 3 % w/v solution. Then chitosan-PVA blends, were prepared by mixing chitosan and PVA solution in different composition. Chitosan-PVA films (thickness 0.16 mm) were prepared from chitosan-PVA solution by casting.

### Modification of Chitosan-PVAFilm with MMA

Chitosan-PVA films were modified with MMA using gamma radiation from  $^{60}\text{Co}$ . The blend films were soaked in four different formulations of MMA in methanol as shown in Table 1 and then irradiated by gamma radiation. Soaking time was varied from 10-30 min and radiation dose was varied from 10-40kGy.

TABLE 1 Composition of different monomer formulation (w/w)

FORMULATIONS	METHANOL (%)	MMA (%)
M1	99	1
M2	97	3
M3	95	5
M4	93	7

**Polymer Loading**

The polymer loading (PL) of the films was determined on the basis of weight gain by the film after the MMA treatment process with radiation (followed by washing with methanol to remove homopolymers). 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 MMA treated film after irradiation (followed by washing with methanol) and  $W_0$  is the weight of the film before MMA treatment. The weight was calculated on dry basis.

**Tensile Properties**

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

**Water Uptake**

Water uptake was measured by soaking the films in distilled water contained in a static beaker at 25°C up to 40 days. The water uptake was determined by the following equation:

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

where  $W_w$  and  $W_d$  are the weights of the wet film and dry film respectively.

**Dynamic Mechanical Analysis**

The thermal properties of films were studied in the temperature range 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.

**Thermogravimetric Analysis**

The thermal stability of the films was analyzed with TGA-50 from Shimadzu, Japan from 25°C to 600°C with a heating rate of 10°C min<sup>-1</sup>, under nitrogen atmosphere with a flow rate of 20 ml min<sup>-1</sup>.

**Fourier Transform Infrared (FTIR) Spectroscopy**

The chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films were characterized by FTIR (ATR) spectrophotometer (8400S Shimadzu Japan) in the range 700- 4000cm<sup>-1</sup>(resolution 4cm<sup>-1</sup>, number of scans: 20 times).

**Scanning Electron Microscopy (SEM)**

The morphological study of the chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films was done by using scanning electron microscopy (SEM) of Model JEOL 6400 at an accelerating voltage of 20 kV. The SEM specimens were sputter coated with platinum.

### Storage of Capsicum annuum 'Bird's Eye':

Capsicum annuum 'Bird's Eye' of known weight were stored in chitosan-PVA film for 13 days, the weight loss of capsicum annuum with respect of control were compared. Weight loss was calculated as follows:

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

where  $W_1$  and  $W_t$  is the initial and final weight (after 't' time) of capsicum annuum.

## RESULTS AND DISCUSSION

### Preparation of Chitosan-PVA Biodegradable Films

Chitosan-PVA films of different composition (thickness 0.16 mm) were prepared by casting. The tensile strength of the films is shown in Table 2. It can be observed that all the blend films have higher tensile strength than pure PVA. Blend films with less than 80 % PVA have higher tensile strength than pure chitosan. The increase of tensile strength could be due to the interaction between OH and  $-NH_2$  groups of chitosan and  $-OH$  groups of PVA. The elongation at break of the films increased with the increase of PVA content in the films. With increasing PVA content in the blend the flexibility of the film increased, therefore elongation at break increased. Considering both tensile strength and elongation at break of the films, chitosan: PVA = 1: 4 (w/w) is selected as the optimum composition of the blend film for further modification. The tensile strength and elongation at break of the chitosan:PVA = 1: 4 (w/w) film was 24 MPa and 20 % respectively.

TABLE 2 The tensile strength and elongation at break of the Chitosan-PVA films

COMPOSITION OF FILM (w/w)		TENSILE STRENGTH (MPa)	ELONGATION AT BREAK(%)
CHITOSAN (%)	PVA (%)		
0	100	18.0	25.0
10	90	19.0	23.0
15	85	20.0	21.0
20	80	24.0	20.0
40	50	25.0	18.0
60	40	25.5	16.0
80	20	26.0	15.0
100	0	20.0	16.0

### Modification of Chitosan-PVA Film with MMA Using Gamma Radiation

To improve the mechanical and thermal properties, chitosan-PVA films were modified with monomer methyl methacrylate (MMA) using gamma radiation. The blend films were soaked in different formulations of MMA (1 %-7 %) in methanol and then irradiated by gamma radiation. Soaking time was varied from 10-30 min and radiation dose were varied from 10-40 kGy. Monomer concentration, soaking time and gamma radiation dose was optimized on the basis of mechanical properties.

### ***Effect of Monomer Concentration on Mechanical Properties of Chitosan/PVABlend Films***

The chitosan-PVA films were soaked in different formulations of MMA (M1-M4) for 20 min and then irradiated by gamma radiation at 30kGy. After 24 hr of radiation, various mechanical properties were measured. The TS values of the irradiated films as a function of monomer concentration are shown in Fig. 1. For 1 % MMA, TS obtained was 30 MPa. TS showed increase with the increase of MMA concentration and reached the maximum of 36 MPa for 3% MMA (M2 formulation) which is 50 % higher than the TS of the film before irradiation. After 3 % MMA, the TS values of the film decreased with the increase of MMA concentration and reached to 28 MPa for 7 % MMA. In the presence of radiation monomer-polymer back bone reaction occurs where the hydroxyl and amino groups of chitosan and PVA may interacts with vinyl radicals of MMA [20]. As monomer concentration increases, more MMA may undergo polymerization with chitosan or PVA and the TS increased. However, at higher MMA concentration TS decreased due to the dominated homo-polymerization rather than monomer-polymer back bone reaction [21-23].

Elongation at break of the irradiated films was studied as a function of monomer concentrations (Fig. 1). It was observed that for all MMA concentration Eb increased after radiation treatment. For 1 % MMA, Eb was found to be 28 %. Eb increased with increase in the percentage of MMA and reached the maximum of 34 % for 3% MMA. After 3 % MMA the Eb values of the chitosan film decreased with increasing MMA concentration and reached to 26 % for 7 % MMA. After MMA treatment using gamma radiation the flexibility of the film increased causing increase of Eb.

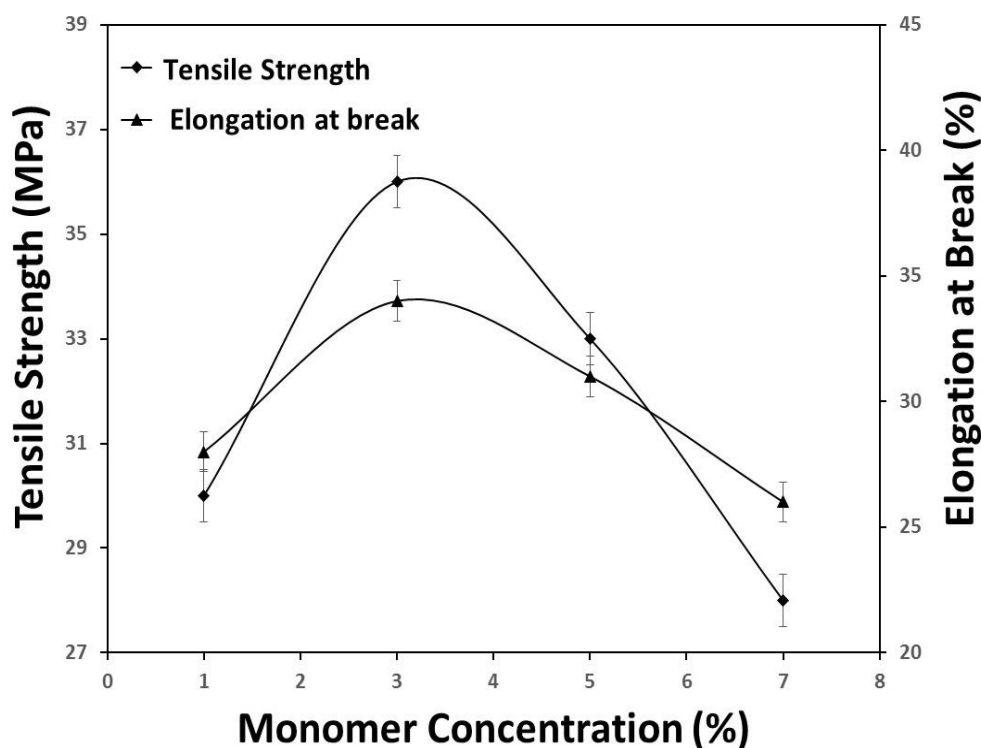


FIGURE 1 Tensile properties of the irradiated films against monomer concentration for 20 min soaking time and 30kGy radiation dose

### ***Effect of Radiation Dose on Mechanical Properties of Chitosan/PVA Blend Films***

On having the highest TS and Eb for 3 % MMA (M2 formulation), the TS and Eb values of the films were studied as a function of radiation dose for 3% MMA at 20 min soaking time. The TS

values of the irradiated films as a function of radiation dose are presented in Fig. 2. For 10kGy TS was found 28 MPa. TS increased with increase in the radiation dose and reached the maximum of 36 MPa for 30kGy radiation dose. After the 30kGy radiation dose TS values of the chitosan film decreased with increasing radiation dose and reached to 32 MPa for 40kGy radiation dose. It is expected that in the presence of radiation some active sites were formed in chitosan, PVA and MMA. With the increase of radiation dose more active site can be generated that can react to form copolymer of chitosan/PVA and MMA. As a result, the TS increased. Nevertheless, at higher radiation dose, homopolymer formation suppresses reaction between chitosan/PVA and MMA. High dose of radiation is also responsible for degradation of chitosan. This occurrence is quite common for natural biopolymers as reported [21, 24-25]. Therefore, at high radiation dose TS of the film decreased.

Elongation at break of the irradiated films was studied as a function of radiation dose (Fig. 2). It was observed that for all radiation doses Eb increased after radiation treatment. For 10 kGy Eb was found to be 26 %. Eb increased with increase in the radiation dose and reached the maximum of 34 % for 30kGy. After 30kGy Eb values of the chitosan film decreased with increasing radiation dose and reached to 30 % for 40kGy.

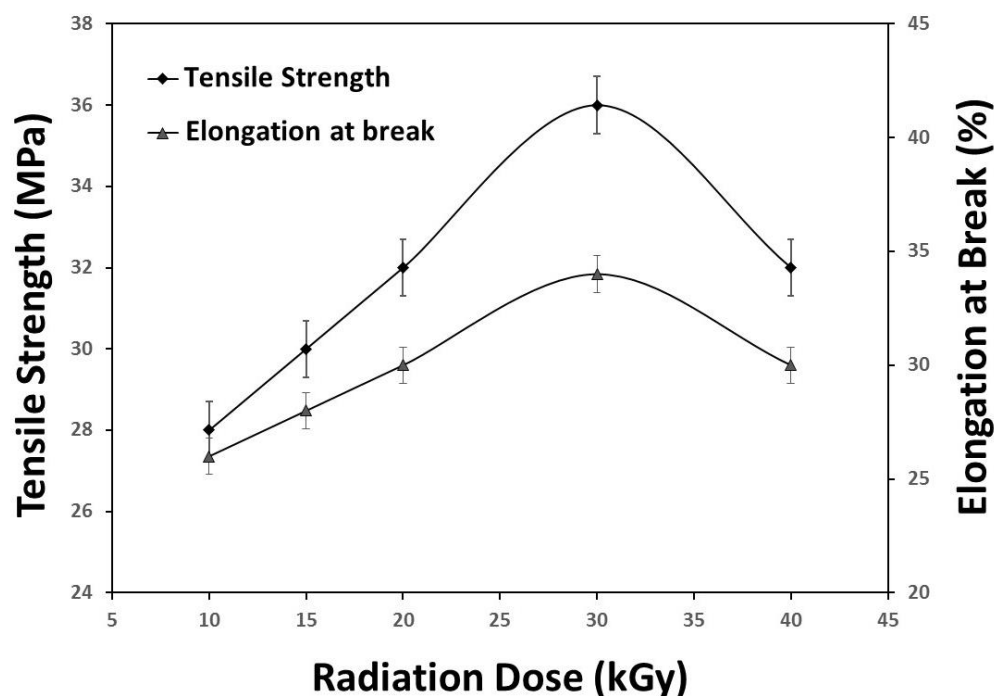


FIGURE 2 Tensile properties of the irradiated films against radiation dose for 20 min soaking time and 3 % MMA concentration

#### ***Effect of Soaking Time on Mechanical Properties of Chitosan/PVA Blend Films***

On having the highest TS and Eb for M2 formulation and 30kGy gamma radiation dose, the blended films were soaked in M2 formulation for different soaking times (10, 15, 20, 25 and 30 min) and then irradiated at 30kGy radiation. After 24 hr of radiation, TS and Eb were investigated. The change of TS of chitosan-PVA films as a function of soaking time are shown in Fig. 3. It was observed from Fig. 3 that for 10 min soaking time TS was found 29 MPa. TS increased with increase in soaking time and reached the maximum of 36 MPa for 20 min soaking time. Increase



of soaking time may cause diffusion of more monomers into the sites of reaction and thus increase the probability of formation of copolymer by reaction between monomer and polymer [26] and therefore the TS of the films increased. However, further increase of soaking time made the film twisted, shrank and hence TS decreased.

Elongation at break of the irradiated films was studied as a function of soaking time (Fig. 3). It was observed that for all soaking time Eb increased after radiation treatment. For 10 min soaking time Eb was found to be 27 %. Eb increased with increase in the soaking time and reached the maximum of 34 % for 20 min soaking time. After 20 min Eb values of the chitosan-PVA film decreased with increase of soaking time and reached to 27 % for 30 min.

Thus the best performance was observed for the chitosan-PVA films soaked in 3% monomer solution for 20 min soaking time and irradiated by 30 kGy radiation dose. The TS and Eb found under this condition were 36 MPa and 34 % respectively.

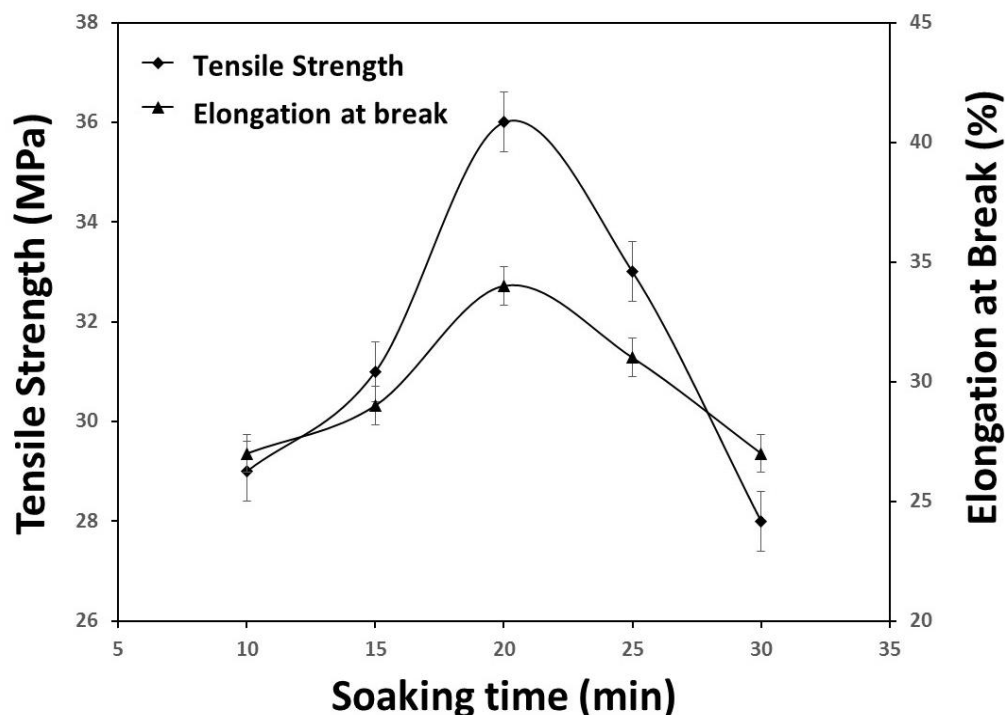


FIGURE 3 Tensile properties of the irradiated films against soaking time for 30kGy radiation dose and 3 % MMA concentration

### Polymer Loading

Polymer loading (PL) values of the radiated films were studied and presented as a function of radiation dose for 3 % MMA at 20 min soaking time in Table 3. For 10 kGy, PL was found 3 %. PL increased with increase in the radiation dose and reached the maximum of 10 % for 30 kGy radiation dose. After 30 kGy radiation dose PL value of the blend film decreased with increase of radiation dose and reached to 8 % for 40 kGy radiation dose. The PL values obtained are in agreement with the mechanical properties.

TABLE 3 Polymer loading of the irradiated blend film at different radiation dose

RADIATION DOSE (kGy)	POLYMER LOADING (%)
10	3
15	6
20	9
30	10
40	8

### Water Uptake

Water uptake of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films were studied for 960 h and the results are presented in Fig. 4. It was observed that chitosan showed lower and PVA showed higher water uptake than the chitosan-PVA film. Irradiated chitosan-PVA film showed lower water uptake than chitosan-PVA film. Figure 4 also shows that after certain immersion time water uptake values of the PVA films started to decrease with increasing immersion time which may be due to the degradation of the swollen PVA film. Degradation of chitosan, chitosan-PVA and irradiated chitosan-PVA films are not significant. Results indicate that the water stability of the PVA films improved after addition of chitosan. Radiation modification further reduced the hydrophilicity of the chitosan-PVA film.

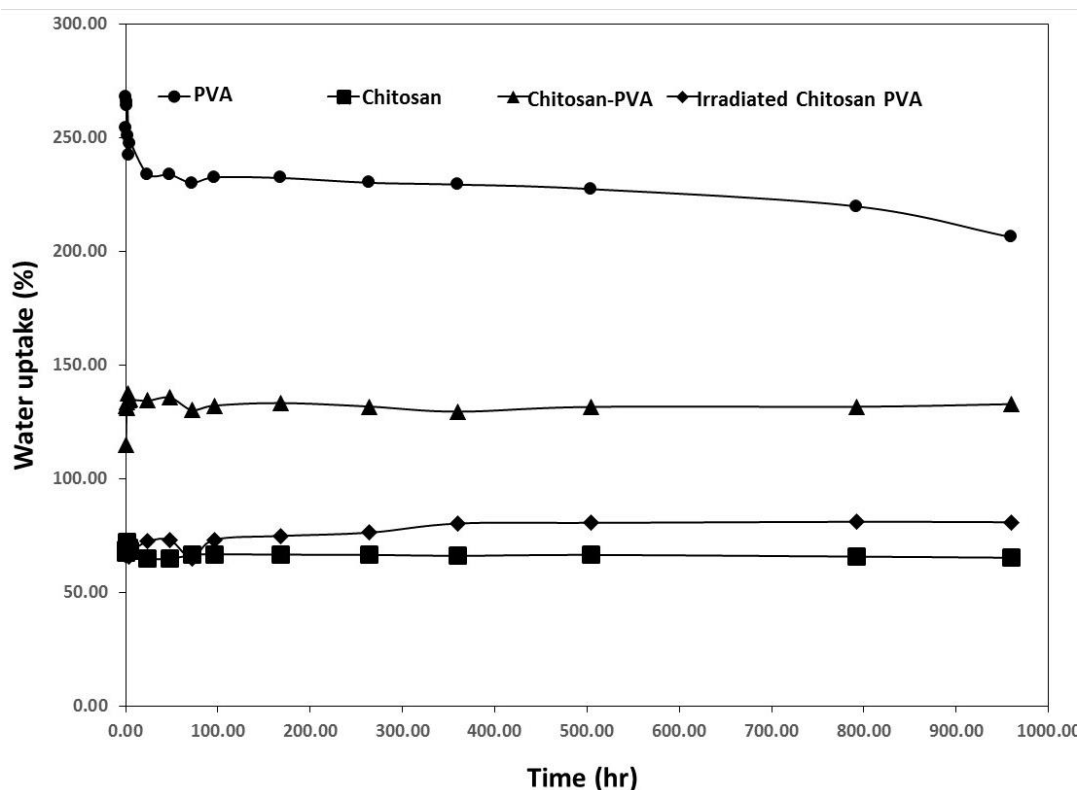


FIGURE 4 Water uptake of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films against immersion time

### FTIR Analysis

Fig. 5 shows the FTIR spectra of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films. The IR spectrum of the chitosan film was similar to previous reports [20]. The chitosan spectrum



showed peaks at 1020, 1075, and 1260  $\text{cm}^{-1}$ , typical peaks of a saccharide structure (due to C–O stretching, O–H bending, and C–N stretching respectively). The peaks at 1548 and 2909  $\text{cm}^{-1}$  corresponded to the N–H bending (amide II) and C–H stretching respectively. A peak at 1722  $\text{cm}^{-1}$  indicates the presence of a carbonyl group. The spectrum of PVA showed peaks at 3272 and 923  $\text{cm}^{-1}$  for O–H stretching and bending respectively. The spectrum of chitosan-PVA film showed characteristic peaks of both chitosan and PVA. The peaks for O–H stretching (3345  $\text{cm}^{-1}$ ), O–H bending (912  $\text{cm}^{-1}$ ), C–O stretching (1033  $\text{cm}^{-1}$ ) and carbonyl group (1713  $\text{cm}^{-1}$ ) that appeared in the spectrum of chitosan-PVA film showed decrease of intensity after radiation modification (spectrum of irradiated chitosan-PVA film). This finding indicates that during the radiation modification the mentioned groups might have interacted with the MMA monomer.

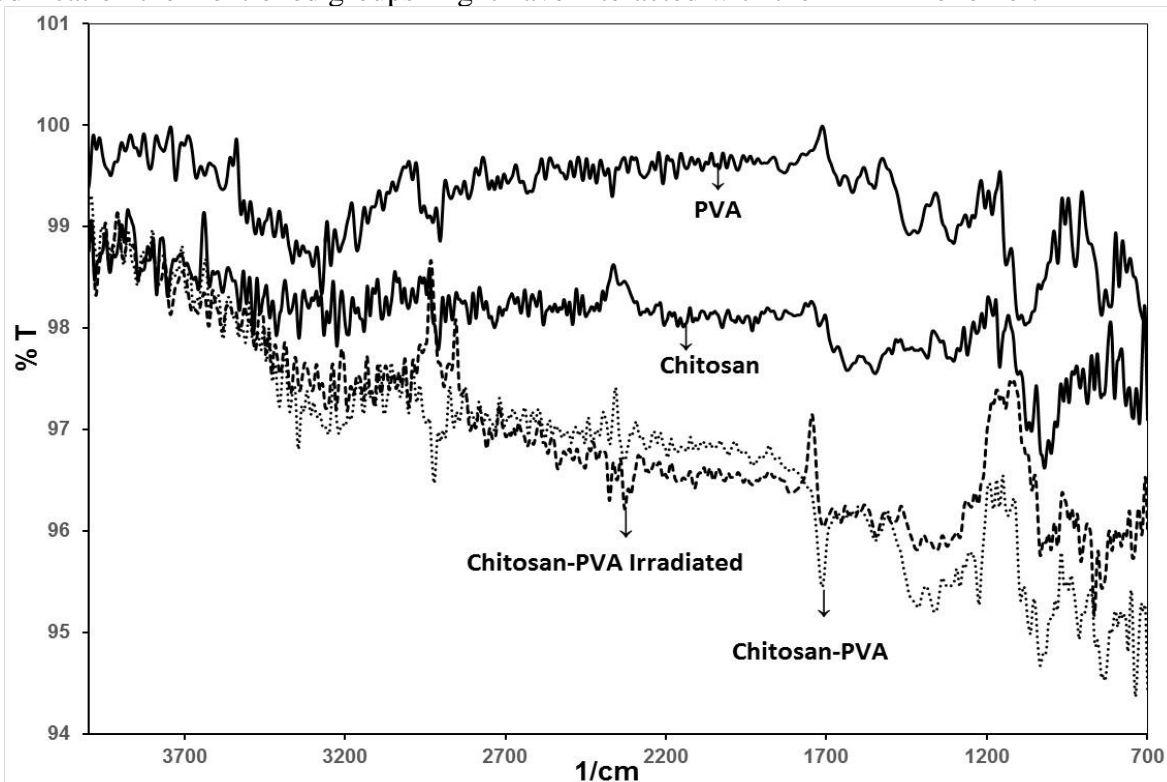


FIGURE 5 FTIR spectra of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films

### Scanning Electron Microscopy Analysis

The scanning electron micrographs of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films are shown in Fig. 6. The SEM micrograph of chitosan showed some unbound microgranules whereas the SEM micrograph PVA showed a smooth surface. The chitosan-PVA blend film showed some degree of heterogeneity. But the irradiated film showed uniform distribution of components in the matrix representing the structural integrity of the film. The soaking of the blend film into the MMA monomer followed by irradiation have caused interaction of polymers of the films with MMA resulting a uniform addition of the monomer on the surface of the polymer film.

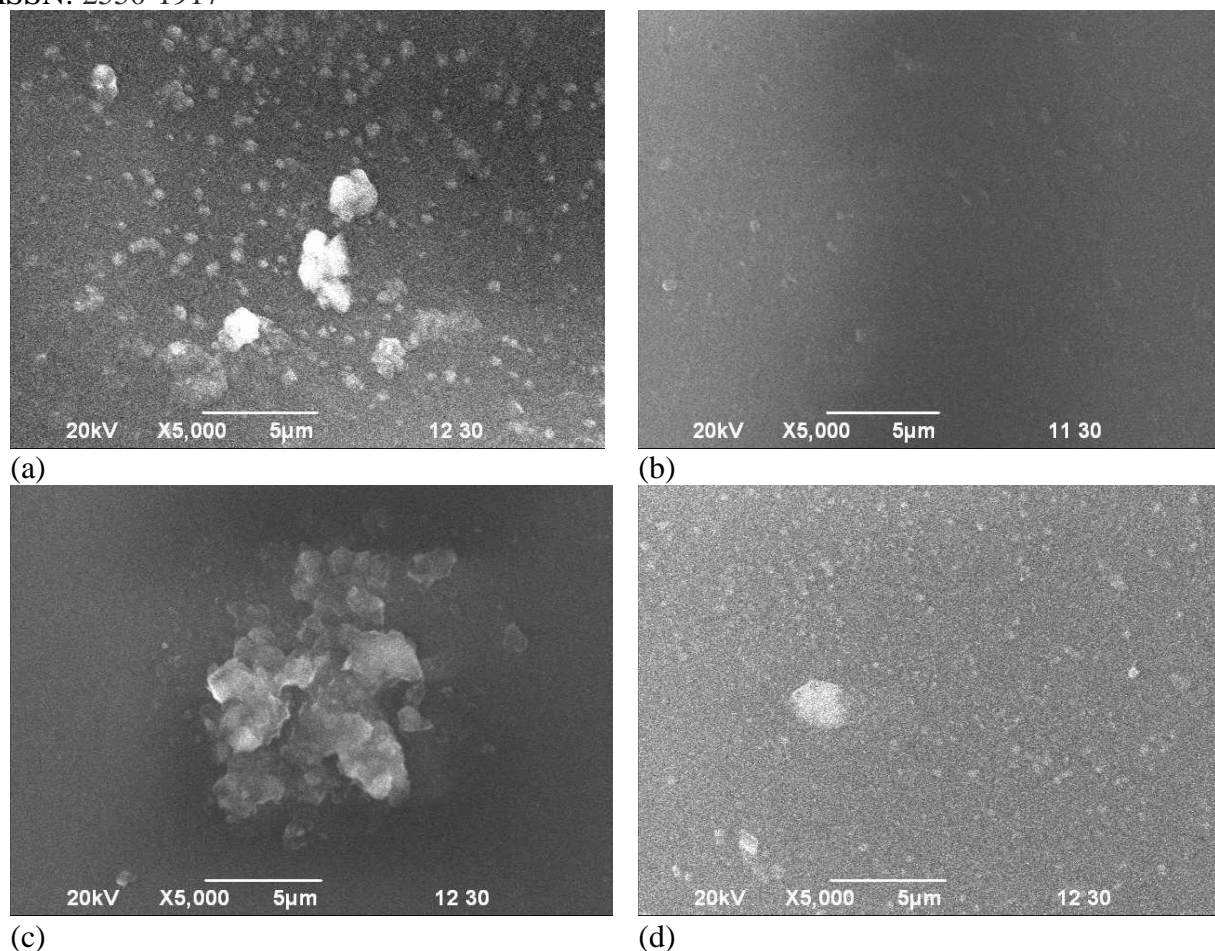


FIGURE 6 The scanning electron micrographs of (a) chitosan, (b) PVA, (c) chitosan-PVA and (d) irradiated chitosan-PVA films

### Thermogravimetric Analysis

Fig. 7 shows the TGA thermograms of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films. It was observed that the weight loss of PVA is lower than chitosan below 370°C but after 370°C the weight loss of PVA is higher than chitosan. The weight loss of chitosan-PVA (both non-irradiated and irradiated) is lower than chitosan below 370 °C and lower than PVA after 370°C. The weight loss of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films at different temperature observed in thermogravimetric analysis are given in Table 4. The TGA data for all films showed two steps in weight loss. For chitosan the two steps are observed below 100°C, ranges of 250-320°C, for PVA the two steps occurred below 140°C, ranges of 290-400°C and for chitosan-PVA (both non-irradiated and irradiated) the two steps occurred are below 140°C, ranges of 260-370°C. The initial weight loss below 140°C is due to the adsorbed water and the major weight loss started above 280°C is related to the char formation [27]. The slightly higher thermal stability of the irradiated film at 600°C than non-irradiated blend film might be due to the rigidity imposed by irradiation.

TABLE 4 Weight loss of the films at different temperatures

SAMPLE FILM	WEIGHT LOSS (%)		
	AT 200°C	AT 370°C	AT 400°C
Chitosan	13	51	55
PVA	6	51	73
Chitosan-PVA	9	46	62
Irradiated Chitosan-PVA	9	48	62

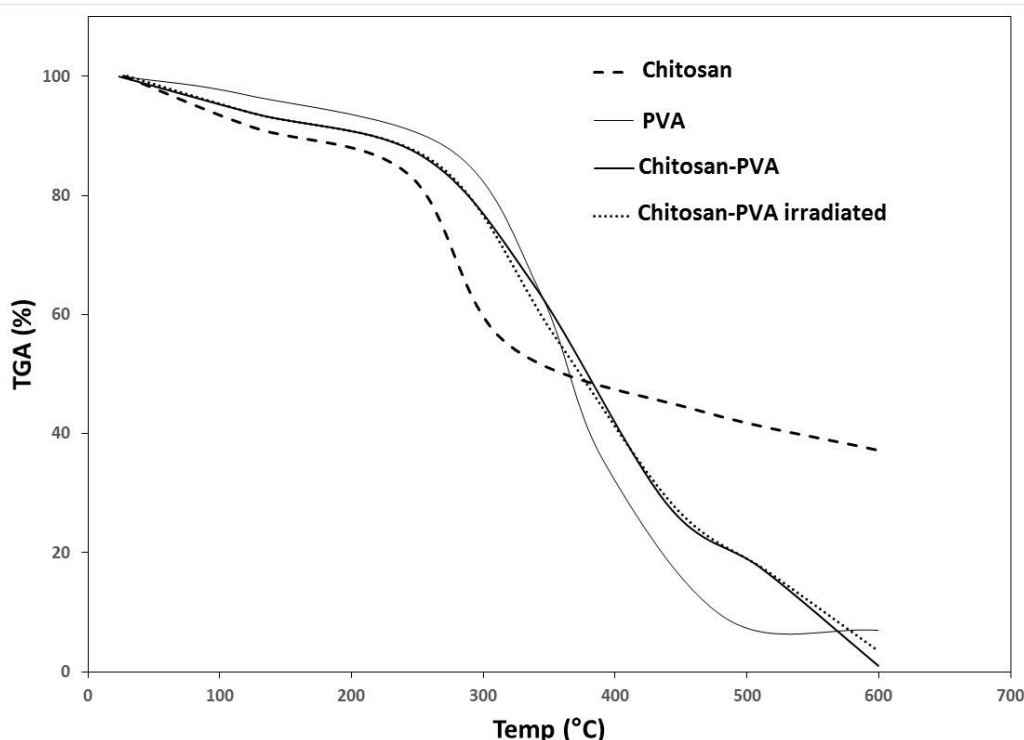


FIGURE 7 TGA thermograms of chitosan, PVA, chitosan-PVA and irradiated chitosan-PVA films

### Dynamic Mechanical Properties

Fig. 8 shows the change in the storage modulus of films. It was observed that the modulus of chitosan film is much higher than the other films. Chitosan film showed the first decrease of modulus from 50-80 °C while the other films showed first decrease of modulus between 26 to 65 °C. These might be due to the intramolecular moisture. Then the modulus increases, reaches a maximum and then decreases again. For pure chitosan modulus increases up to 145 °C and then storage modulus started to decrease. This transition, called the  $\alpha$ -transition, ( $T_\alpha$ ), around 145 to 177 °C, is defined as glassy region at which chitosan changes its behavior from being 'glassy' to being 'rubbery' [25]. For PVA the glass transition region started around 116 °C, for chitosan-PVA film the glass transition region started around 136 °C and for MMA treated irradiated chitosan-PVA film the glass transition region started around 124°C. An important finding of DMA studies is that the 2<sup>nd</sup> transition temperature ( $t_g$ ) of PVA increased after blending with chitosan which might be useful for some applications.

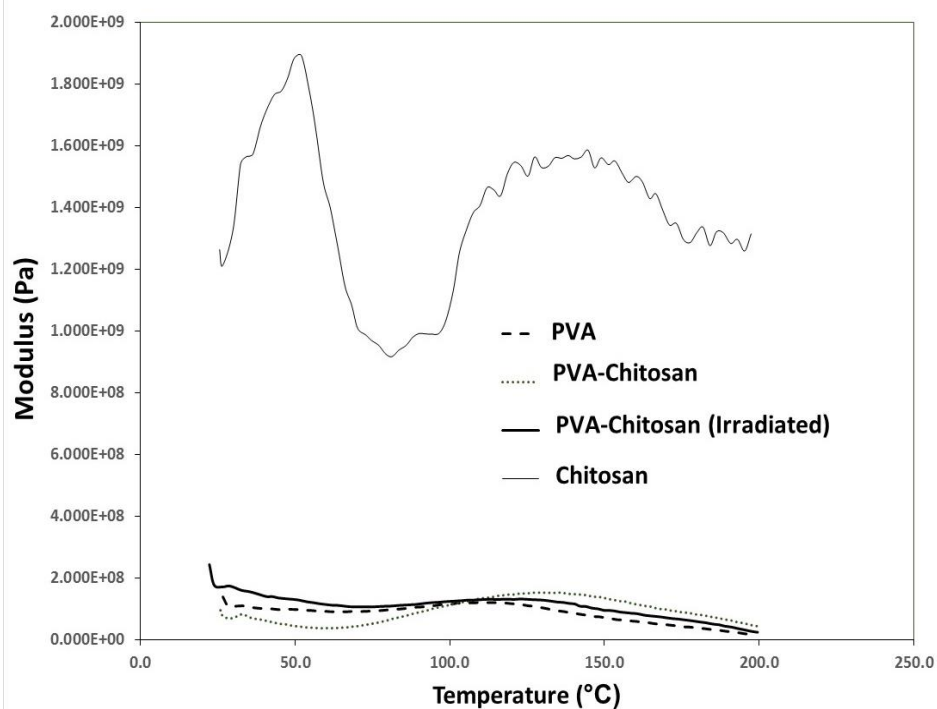


FIGURE 8 Storage Modulus as a function of temperature for different films.

#### Storage of Capsicum annuum 'Bird's Eye':

Capsicum annuum 'Bird's Eye' of known weight was stored in chitosan-PVA film for 13 days. The weight loss of the capsicum annuum stored in the chitosan-PVA films is compared with control in Fig. 9. It is observed that the capsicum annuum stored in chitosan-PVA film showed less weight loss than control. The capsicum annuum stored in irradiated chitosan-PVA film showed lower degradation than the capsicum annuum stored in chitosan-PVA film. The result indicates that the chitosan-PVA film can improve the shelf life of capsicum annuum. This study was carried out to investigate the potential of the application of the prepared films as bio-packaging for vegetables.

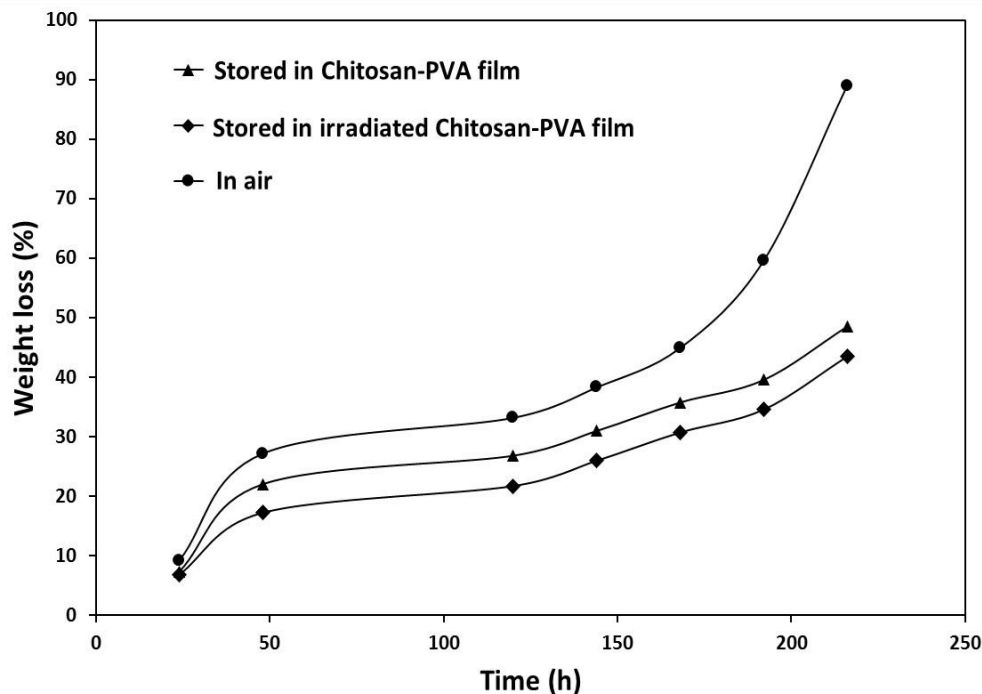


FIGURE 9 The weight loss of capsicum annum stored in chitosan-PVA film is compared with control

### CONCLUSION

In present study different composition of chitosan-PVA blend films (thickness 0.16 mm) were prepared by casting method. Optimum composition (chitosan: PVA = 1: 4) for the film was selected based on mechanical properties. The tensile strength (TS) and elongation at break (Eb) of the film at this composition was 24 MPa and 20 % respectively. The blend films were modified with monomer, methyl methacrylate (MMA) using gamma radiation. Monomer concentration was varied from 1-7 %, soaking time was varied from 10-30 min and radiation dose were varied from 10 kGy-40 kGy. Mechanical properties of the radiation modified films were investigated. The best performance was observed for the chitosan-PVA films soaked in 3% monomer solution for 20 min soaking time and irradiated by 30 kGy radiation dose. The TS and Eb found under this condition was 36 MPa and 34 % respectively. Water uptake of the films indicates that radiation modification reduced the hydrophilicity of the chitosan-PVA film. An important finding of DMA studies is that the 2<sup>nd</sup> transition temperature ( $t_g$ ) of PVA increased after blending with chitosan. The TGA data for all films showed two steps in weight loss, the initial weight loss below 140°C is due to the adsorbed water and the major weight loss started above 280°C is related to the char formation. The structural and morphological features of films were investigated using FTIR and SEM. FTIR analysis showed that the interaction of blend film with monomer might have occurred through the hydroxyl and carbonyl groups. SEM analysis showed that the surface of the blend film became smooth and homogeneous after radiation modification.



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