PHYSICOMECHANICAL PROPERTIES OF PHOSPHATE GLASS CONTAINING CHITOSAN FILMS

F. Ferdoush[1], * Mubarak A. Khan[2] and Ahmad Ismail Mustafa[3]

[1]Department of Arts and Sciences, Ahsanullah University of Science and Technology,
Dhaka-1208, Bangladesh,

[2]Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology,
Bangladesh Atomic Energy Commission, GPO Box No. 3787, Dhaka 1000, Bangladesh,

[3]Department of Nutrition and Food Engineering, Daffodil International University,
Dhaka 1207, Bangladesh.

Abstract: *In this study, 5% phosphate glass (PG) containing chitosan film was grafted with Polyethylene Glycol (PEG) using UV-radiation. A series of formulation was developed with PEG in methanol. In order to optimize the grafting conditions, the effect of PEG concentration and different radiation doses were studied. Tensile strength (TS), elongation at break and thermal stability of grafted films were studied. The highest TS was found to be 13.80 MPa with 100% PEG, 0% methanol using 2% photoinitiatior at 3 minutes soaking time at 30th UV passes in 5% phosphate glass containing chitosan film. The physico-mechanical properties of prepared films were improved by grafting with PEG with the aid of UV radiation. The DTA/TG study also showed that treated 5% phosphate glass containing chitosan film was more thermally stable than untreated film. The water uptake behaviors of these films were also studied.*

Keywords: *Chitosan, Phosphate glass, PEG, PL, TS, Eb.*

Introduction

Chitosan is a linear polysaccharide obtained by deacetylation of a naturally occurring polymer chitin. It consists of 2-amino-2-deoxy- (1-4)-β-D-glucopyranose residues (D-glucosamine units) and has a small or moderate amount of *N*-acetyl-D-glucosamine units[1]. Chitosan is non-toxic, biocompatible and biodegradable cationic polymer and find applications in pharmaceutical, medicine and food industry. Keeping in mind renewable resources of this polymer and its biodegradability and biofunctionality, it would be attractive in some other fields of applications including water-treatment materials, personal care products and polymeric surfactants[2, 3]. However applications of chitosan are limited by poor solubility. Chitosan is soluble in acidic aqueous solutions only where the amino groups are protonated.

However, the poor physical/mechanical properties and high degree swelling of chitosan film in an aqueous system limit its practical application. One way to overcome these limitations effectively and conveniently is by creating chemical cross-linking. On the other hand, formation of organic-inorganic composite film provides properties of chitosan and other biomaterials. Recently, grafting of organophosphorus coupling agents (OPCAs) on preformed inorganic supports or in-situ formation of the inorganic part in presence of organophosphorus reagents offers a potential alternative to the silicon- or titanate- based coupling agents. Based on the ability of phosphate ions to exchange with

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***Corresponding author:** M.A. Khan, Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, GPO Box No. 3787, Dhaka 1000, Bangladesh. E-mail: makhan.ins@gmail.com the phosphate ions on Hydroxyapatite (HAp) crystals, any polymer containing a number of phosphate or phosphoric acid groups is expected to have higher affinity for the Hap particles [4]. Moreover, the phosphate- containing polymers are expected to have higher mechanical properties and biocompatibility [5] . In the preparation of bio analogue composites, organophosphonate- or phosphate-based coupling/ anchoring agents are being extensively used by the researchers to improve the compatibility between inorganic nanoparticles and polymer matrix [6-10] .

Chitosan is mostly applied as a food additive or preservative, and as a component of packaging material, not only to retard microbial growth in food, but also to improve the quality and shelf- life of food[11]. Many chitosan derivatives are water soluble in a wide range and show unique biological activities and physicochemical properties[12]. Poly (ethylene glycol) (PEG) is regarded as one of the most suitable graft-forming polymers because of its unique properties including solubility in water and organic solvents, low toxicity, good biocompatibility and biodegradability [13]. PEG is one of the few synthetic polymers approved for internal use in food, cosmetics, personal care products and pharmaceutical[14]. Several publications reported modification of chitosan with PEG of different molecular weight[1, 15, 16]. N-substituted chitosan derivatives only were obtained in these studies. Addition of food-grade plasticizers (PEG) to ilm-forming, the molecular rigidity of a polymer is relieved by reducing the intermolecular forces along the polymer chain. The plasticizer improves flexibility and reduces brittleness of the film [17.]

Naturally occurring polymers absorb solar radiation and undergo photolytic, photo-oxidative and thermal-oxidative reactions that result in the degradation of the material[18, 19]. The degradation suffered by bio-polymeric materials can lead to a loss of mechanical properties, which limit their performance. In particular, in sunlight, the ultraviolet radiation determines the useful lifetime of many materials. In this experimentation, using phosphate glass with chitosan and Phosphate glass (PG) developed new blended film. Degradable phosphate glass fiber reinforced polymer matrices: for internal fracture fixation is of great interest, as they would both eliminate the problem of stress shielding and obviate the need for a second operation to remove fixation devices. Preliminary investigations for the production of degradable fiber reinforced polymer composite materials are detailed. Composites were produced of phosphate invert glass fibers of the glass system P_2O_5-CaO-MgO-Na_2O-TiO_2, which showed a low solubility in previous work. The fibers were embedded into a matrix of a degradable organic polymer network based on methacrylate-modified oligalactide. Fracture behavior, bending strength and elastic modulus were evaluated during 3-point bending tests and the fracture surface of the composites was investigated using a scanning electron microscope. Short-term biocompatibility was tested in an FDA/EtBr viability assay using MC3T3-E1 murine pre-osteoblast cells and showed a good cell compatibility of the composite materials. Results suggested that these composite materials are biocompatible and show mechanical properties which are of interest for the production of degradable bone fixation devices[20]. By using Phosphate glass the performance of chitosan/phosphate glass blend film was improved, because it is highly resistant to solvent and forms a tough, clean film that have high tensile strength.

The aim of the present work was to carry out a systematic study of chitosan/phosphate glass film with different compositions, prepared by varying the % ratios of PG with chitosan. The physicochemical properties of the films were examined by FTIR. Also, the water uptake, polymer loading, tensile strength, elongation break, and the in *vitro* degradation of the blended film, treated and untreated by UV pass were fully investigated. In this study, cross-linking was also studied after treated film by UV pass. This scientific investigation was designed for developing the chitosan/phosphate glass blend that would be used in different medical field especially for controlled drug delivery and scaffold material for bone tissue engineering.

Materials and methods

Chitosan as Poly-(1-4)-2-Amino-2-deoxy-ß-D-glucan, $(C_6H_{11}NO_4)_n$, Mw = $(160.9)_n$, was extracted from fresh water Prawn Shells collected from Macro brachium malacolmsoni, Bangladesh. Methanol (CH_3OH), sodium hydroxide (NaOH) and photo initiator (Darocur-4043) were supplied by Merck (Germany). BDH chemicals limited, England, supplied acetone, acetic acid and hydrochloric acid.

Chitosan was extracted from prawn shell waste [21]. Chitosan was obtained by deacetylation of chitin using NaOH (chitin:NaOH = 1:20,w/w at 100 ^{0}C) for 3.5hrs. After this process, solid was separated from the alkali and were extensively wash with distilled water to remove traces of alkali. The resultant solid was dried in a vacuum oven at 50 ^{0}C for 24 hrs. Chitosan was extracted in this way from prawn shell waste. All the membranes or films of pure chitosan, phosphate glass and chitosan/phosphate glass blends were prepared by using solution casting technique. Pure Chitosan films were prepared from 2% Chitosan solution dissolved in 2% glacial acetic acid solution. Films were prepared by casting the solutions on Silicon sheets [22]. The Prepared films of pure chitosan were dislodged carefully, and then subjected to further drying under vacuum desiccators for 2 days. The same process (as 2% chitosan solution blend with PEG/PG) was followed for the preparation of pure phosphate glass film except the solution was stirred magnetically at 70°C. The blend films of chitosan/phosphate glass were prepared using the solution casting method. Table-1; Chitosan and phosphate glass solution were easily can mixed in different weight ratios. The mixture of both polymer aqueous solutions with different weight ratios were cast on a silicon sheet. The film thickness ranged 0.2±0.5 mm.

Table I. Casting conditions for the blend films

Condition no.	Blend ratio chitosan /phosphate glass (w/w)	Casting temperature (^{0}C)
1	0.99/0.01	30
2	0.97/0.03	30→ 35
3	0.95/0.05	35
4	0.90/0.10	35→ 40

The blend films of chitosan/phosphate glass were prepared using the same technique as pure chitosan films. The mixture of both polymer aqueous solutions with different weight ratios (0.99/0.01, 0.97/0.03, 0.95/0.05 and 0.90/0.10, chitosan/phosphate glass) were cast on a silicon sheet (Table-l). The film thickness ranged 0.2±.05 mm.

Table 2: Physico-mechanical properties of chitosan/phosphate glass blended films

Blend	% of PG in chitosan	TS MPa	Eb%
B1	33.3	5.3	107.7
B2	60.0	5.4	105.5
B3	71.4	7.80	37.19
B4	83.3	4.1	49.81

First, the mixtures of chitosan and phosphate glass with different ratios were magnetically stirred at 50°C for 150 min and then kept at room temperature for 60 min. Table-2 represents the four different composition of blend with their physico-mechanical properties. Higher composition of phosphate glass films are softer and can easily absorb moisture. These are impossible to handle. So, further investigation for physico-mechanical properties of 1%, 3%, 5% and 10% phosphate glass containing chitosan film was done. Lower phosphate glass content (1%) films were brittle and cracked during drying. Therefore, chitosan /phosphate glass film which contained 5% phosphate glass was suitable for optimization.

Table 3: Composition of formulations

Formulations	PEG (%)	Photo initiator (%)	Me OH (%)
F1	3	2	95
F2	30	2	68
F3	50	2	48
F4	100	2	0

Several formulations were prepared with this solution, differencing the concentration of poly ethylene glycol (PEG) in methanol under UV-radiation. For grafting on chitosan/ phosphate glass films, four formulations, named F1-F4, were prepared in the presence of a photo initiator, Darocure-1664. Table-3 presents the compositions of the formulations. Better grafting means better cross-linking of PEG with polymer was also observed.

The cured films were then subjected to various characterization tests such as tensile properties (TS and Eb), PL, water uptake and gel content. Tensile properties of the cured films were measured with a universal testing machine (Instron model 1011, UK). The crosshead speed and gauge length were 10mm/min and 20mm, respectively with a load range 500N, efficiency is within ±1%. The polymer loading of different soaking formulations with the film is determined on the basis of weight gain by the film after the entire treatment process. Polymer loading, PL was determined by the following equation.

$PL (\%) = [(W_t - W_o)/W_o] x100.$

Where, W_t is the weight of the treated (dry) film and W_o is the weight of the untreated (dry) film. The water uptake of the treated and untreated films is periodically (15sec, 30sec and 60sec or 1 min) monitored upto 1 min to find the profile of water uptake. Water uptake is determined using the following equation.

$W_g = [(W_a - W_o)/W_o] x100.$

Where W_g is % of weight gained by the sample due to water absorption, was weight of the sample after water treatment and W_o is weight of the dry sample before water treatment. The thermal test of the films was taken using computer controlled TG/DTA 6300 system controlled to an EXSTAR 6000 STATION, Seiko Instrument, Inc. Japan. The TG/DTA module uses a horizontal system balance mechanism. The FTIR spectroscopy of chitosan films was performed by FTIR spectrophotometer (Paragon 500Model, Perkin-Elmer, Beaconsfield, Bucking hamshire, UK) in the wave number range 400-4000 cm^{-1} with a resolution of 4 cm^{-1}. The FTIR spectrum was taken in a transmittance mode.

Results and discussion

Optimization of grafting condition of polyethylene glycol on chitosan/phosphate glass blended film
Polymer loading (PL)

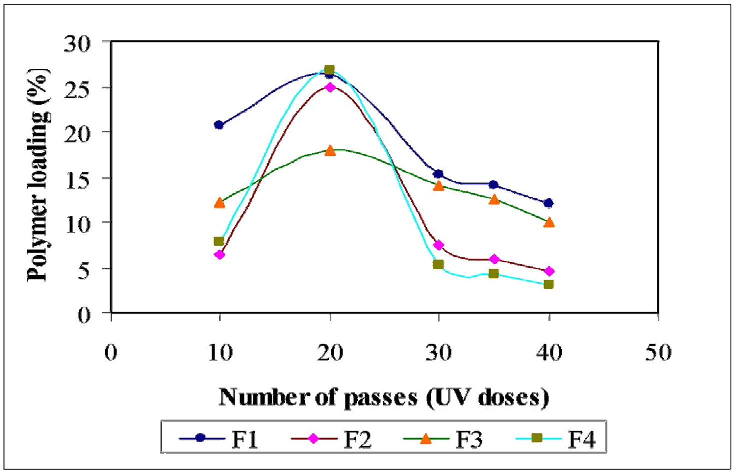

Figure 1: Polymer loading of chitosan/phosphate glass blended film which contained 5% phosphate glass against number of passes (UV doses) with respect to PEG formulations (F1, F2, F3, F4) at 3 minutes soaking time

Polymer loading of the chitosan/ phosphate glass blends (B3 composition of the blend) using the formulations (F1-F4), at 3 minutes soaking time, under UV radiation was investigated and presented in Fig.1. From Fig.1, it is observed that PL values increases with UV radiation intensity and after attaining a maximum value, it begins to decrease. The PL values decreased with further increase in radiation intensity. This may be caused by the radiation degradation at higher UV doses[23]. The maximum value of chitosan/ PG blend was found to be 26.70% using F4 formulation at 20th UV pass.

Tensile strength (TS)

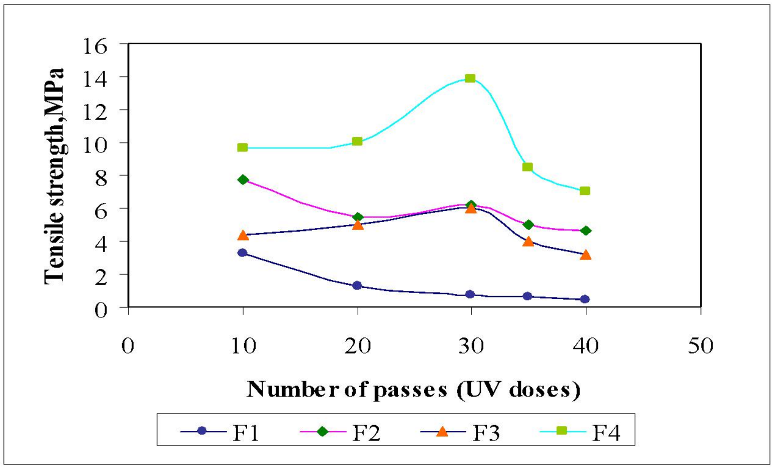

Figure 2: Tensile strength of chitosan/phosphate glass blended film which contained 5% phosphate glass against number of passes (UV doses) with respect to PEG formulations (F1, F2, F3, F4) at 3 minutes soaking time

Variation of tensile strength of grafted blend (B3 composition of the blend) with UV radiation doses, in the prepared formulation at 3 min soaking time is presented in Fig.2. This figure reveals that TS values increased with UV radiation doses up to a certain limit and then decreased. It is observed that F4 formulation shows the highest TS value 13.80 MPa at 30th UV-pass on chitosan/phosphate glass blend film, which contained 5% phosphate glass. At 25 passes, TS was found to decrease more than that of the original values. The maximum value of tensile strength reached to 8.32MPa at 7.93% concentration of PEG and 28.79% volume of PLA/71.2% chitosan. From this investigation it is clearly found that UV radiation has a weak effect on chitosan, PG and their blend. TS increase with increasing irradiation doses up to a certain limit but after that, they decrease due to opposite phenomenon such as photo cross-linking and photo degradation that were taking place simultaneously under UV radiation. In lower doses, free radicals are stabilized by combination reactions; as a result, photo cross-linking or intercross-linking occurs between the neighboring polymeric molecules. The higher the number of active sites generated on the polymeric substrates, the greater is the cross-linking efficiency. At higher UV radiation (above UV passes), TS values decrease, which may be associated with the photodegradation of polymer backbone at higher UV does. At higher radiation, main chain may be broken and polymer may degrade into fragments. As a result tensile properties decreased with increasing higher UV doses. High radiation doses cause loss in strength due to primary bond breakage in the polymer constituents[25, 26, 27].With the polyethylene glycol (PEG) treatment, the TS value of treated Chitosan/PG film increases which is due to the cross-linking of the amino group in chitosan with hydroxyl group of polyethylene glycol. Similar result was also found, when PEG was blended with chitosan-silica films. Blending with PEG changes the properties of the film. The tensile strength tends to decline with the addition of PEG 0.05g and more than that mass shows constant in the tensile strength. It may be attributed to the strong inner-stress existing in the film[30].

Elongation at break (Eb)

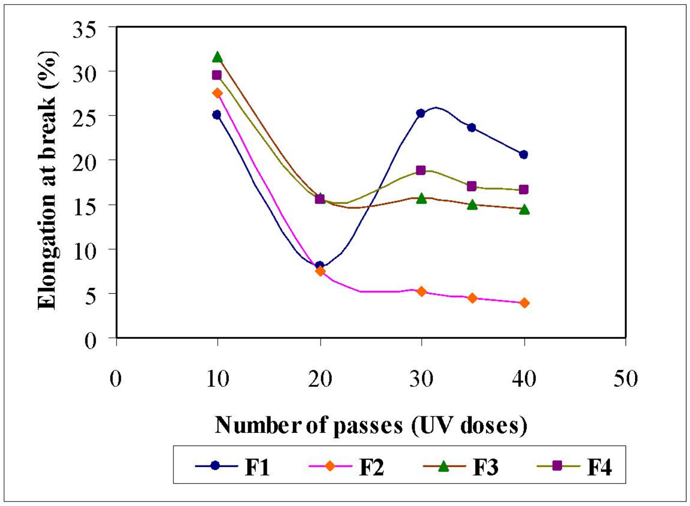

Figure 3: Elongation at break of chitosan/phosphate glass blended film which contained 5% phosphate glass against number of passes (UV doses) with respect to PEG formulations (F1, F2, F3, F4) at 3 minutes soaking time.

In Fig. 3, % elongation at break of the PEG treated chitosan/PG films are depicted against the number of UV radiation intensities for 3 min soaking time and shows an unlike pattern to the tensile strength. From the Fig.3 it is observed that F3 formulation shows the highest Eb percent 31.54 at 10th UV-pass on chitosan/PG blend film (B3 composition blend). A reasonable elongation is an important mechanical property in the application of polymer. Observing the figure 3, it is found that the value of elongation is decreasing with increasing the value of radiation intensity unlike tensile strength. This results are in agreement with the work done by Nasreen et al., 2016 and Khalil et al., 2006 where they studied the cured polymeric film prepared from chitosan-gelatin blend [31, 32]. Polyethylene glycol gave the highest Eb value up to a certain limit and after this produces brittle film that break easily during stretching [31]. On the other hand methanol increases the elasticity and imparts some flexibility. So it is clear, that TS and Eb are very much dependent on the PEG of the formulations~~.~~

Water uptake

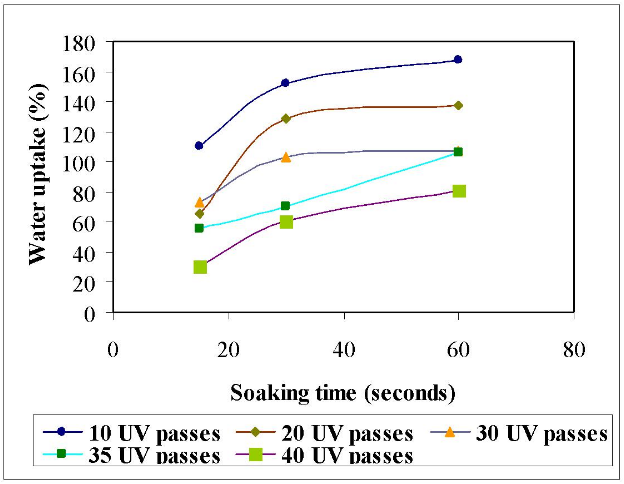

Figure 4: Water uptake of chitosan/phosphate glass blended film which contained 5% phosphate glass against soaking time (second) with respect to 10, 20, 30, 35 and 40th UV passes in PEG formulation (F1).

The water-uptake curve as a function of chitosan content and type of blends are shown in Figure 4-7. Percentage of water uptake of 2% chitosan,2%chitosan/1,3,5 &10% PG blend and 2% chitosan/5% PG in (F1,F2,F3 &F4) formulations are done against various immersing time (15,30 and 60 seconds).

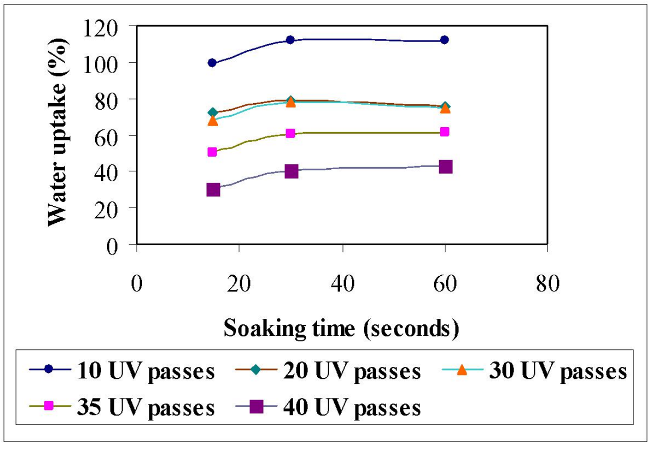

Figure 5: Water uptake of chitosan/phosphate glass blended film which contained 5% phosphate glass against soaking time (second) with respect to 10, 20, 30, 35 and 40th UV passes in PEG formulation (F2)

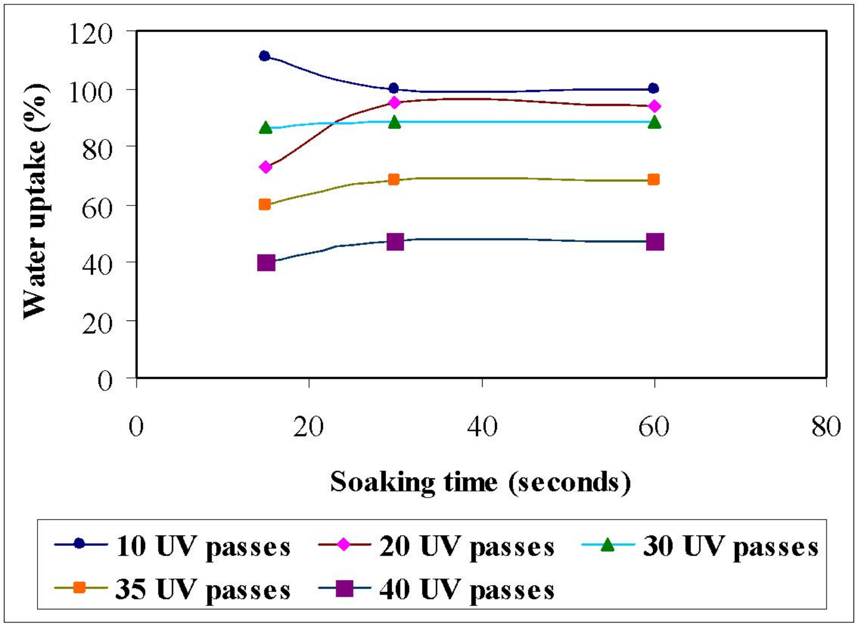

Figure 6: Water uptake of chitosan/phosphate glass blended film which contained 5% phosphate glass against soaking time (second) with respect to 10, 20, 30, 35 and 40th UV passes in PEG formulation (F3)

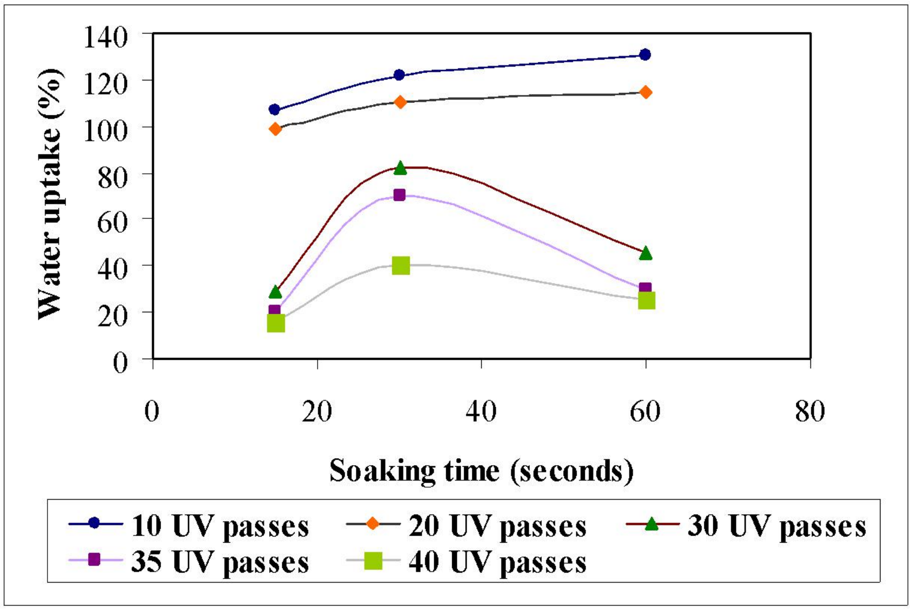

Figure 7: Water uptake of chitosan/phosphate glass blended film which contained 5% phosphate glass against soaking time (second) with respect to 10, 20, 30, 35 and 40th UV passes in PEG formulation (F4)

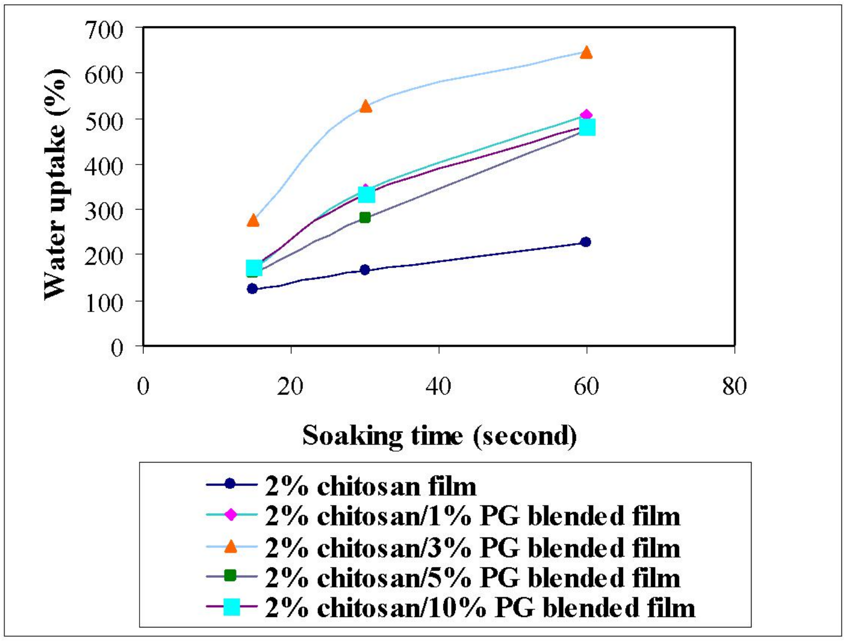

Figure 8: Water uptake of 2% chitosan, 2% chitosan/1% phosphate glass, 2% chitisan/3 % phosphate glass, 2% chitosan/5% phosphate glass and 2% chitosan/10% phosphate glass blended films against soaking time in (second)

It is observed from Fig.8, for the sample during first few seconds, water uptake is faster and it then slows down and attains a plateau almost. This was an expected result since chitosan is hydrophilic and the aliphatic polyesters are hydrophobic. Similar results are reported in the literature for polyester blends with other natural origin polymers like starch[31, 33]. This is primarily happened due to the presence of amine and hydroxyl groups on the chitosan moiety, which is the most probable site for accommodation of additional water. The water uptake percentage is highest for chitosan/PG blend which contain 3% PG (untreated) and least for the chitosan/PG blend which contained 5%PG (treated). Higher water uptake of the treated films may be due to the provision of more intra and inter molecular space in the grafted polymer structure. The highest water uptake percent after 1 min is 654% for chitsan/3% PG blend film (untreated), 228.40% for chitosan film and 167% for chitosan.5% PG blended film (treated) in formulation F1 at 10th UV-passes. The lower water absorption of cured chitosan is due to the cross linking of PEG with chitosan. More cross-linking lowers the void space within the polymer structure to get into the water in it. But higher UV- pass may cause degradation of the structure of the polymer. This observation was also found when glutaraldehyde was added, it decreased the average size of the polymer particle and then decreased the free volume and voids by increasing the affinity between the starch, chitosan with the cross linking agent[34]. Due to the decrease in free voids, water absorption capacity of the blend prepared in the presence of the cross linking agent and apply of UV radiation decreases.

Thermal analysis

The TG, DTA and DTG curves of 2% pure chitsan film were observed. The mass is continuous losing having slower initial rate and ending is the faster rate. The lighter substances were removed initially and then heavier materials were removed. Two steps can be observed in the TG-curve: the first one at about 12.6% mass loss was accompanied by endothermic effect and attributed to the evaporation of water absorbed in the inner polymer. The second one, beginning at about 167.1^{0}C and ending at 334.9^{0}C was 50% mass loss and indicated vaporization and burning of volatile compounds produced from the thermal degradation of polymeric chain. At temperature above 257.4^{0}C, significant change was observed in the course of the structure of the material and change of the mechanism of its thermal degradation process. . Four endothermic DTA peaks were observed at 99.0^{0}C, 183.7^{0}C, 261.5^{0}C and 460.5^{0}C respectively, however an exothermic peak was observed at 286.8^{0}C. The 1st peak at 99.0^{0}C is due to removal of moisture, 2nd peak is for lighter material and 3rd peak for heavier material, 4th peak for heat evolved and 5th peak for degradation. Three DTG peaks were also found at 99.4^{0}C, 287.7^{0}C and 418.4^{0}C respectively, corresponding to lighter material and heavier material. DTG curve of 2% chitosan film depicts that the maximum degradation occurs at the temperature 287.7 ^{0}C with the rate of 0.183 mg/min.

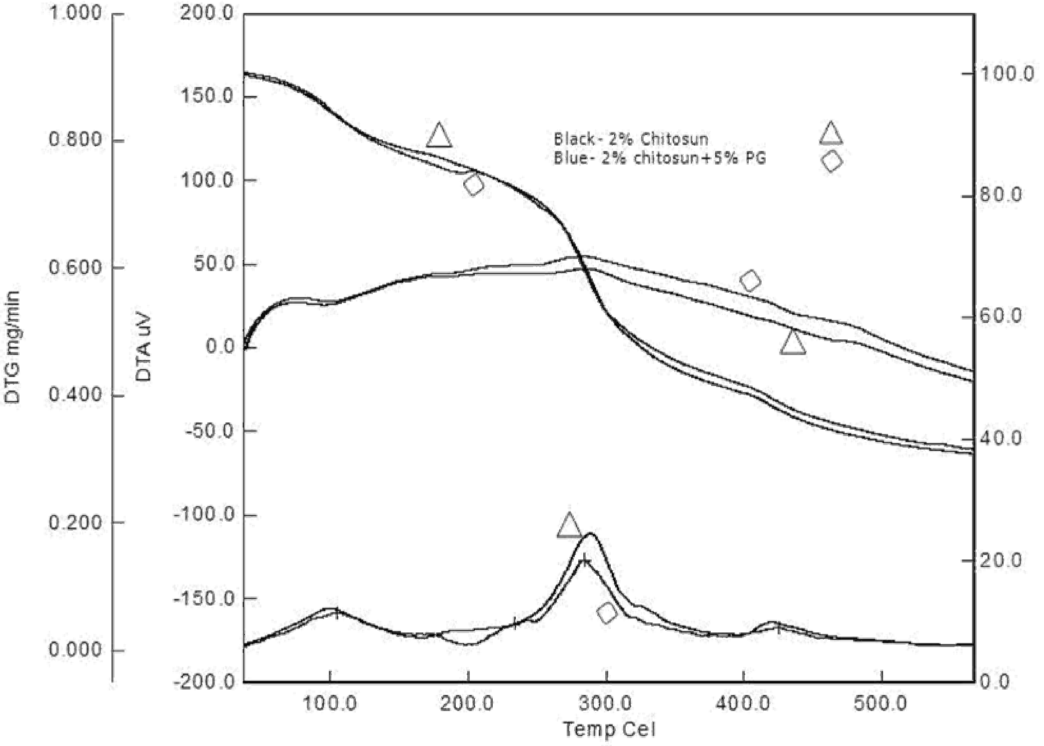

Figure 9: TG, DTA and DTG curves of 2% Chitosan, 2% chitosan /5% phosphate glass blended films.

Fig.9. Shows the TG, DTA and DTG curves of 2% chitosan/5% Phosphate glass blended films. The TG curve shows an initial 16.2% loss corresponding to its moisture content. Then the mass loss is continuous, having slower initial rate and faster ending rate. The lighter substances remove initially and then heavier material removed. Two steps can be observed in the TG-curve: the first one at about 16.2% mass loss was accompanied by endothermic effect and was attributed to the evaporation of water absorbed in the inner polymer. The second one, beginning at about 198.0^{0}C and ending at 324.8^{0}C was connected with 50% mass loss and was indicated for vaporization and burning of volatile compounds produced from the thermal degradation of polymeric chain. At temperature above 253.1^{0}C, significant change was observed in the course of the structure of the material and change of the mechanism of its thermal degradation process. Four endothermic DTA peaks were observed at 101.7^{0}C, 194.0^{0}C, 261.1^{0}C and 432.1^{0}C respectively, however peak was observed at 284.9^{0}C. The 1st

peak at 101.7^{0}C was due to removal of moisture, 2nd peak was one exothermic for lighter material and 3rd peak for heavier material, 4th peak for heat evolved and 5th peak for degradation. Four DTG peaks were also found at 104.5^{0}C, 234.1^{0}C, 284.9^{0}C and 425.6^{0}C respectively, which are correspond to lighter material and heavier material. DTG curve of 2% chitosan/5% PG blended film depicts that the maximum degradation occurs at the temperature 284.9^{0}C with the rate of 0.141^{0}C mg/min.

The stability of 2%chitosan is better than that of 2%/5% PG blended films. Here for 2% chitosan film onset temperature 257.4^{0}C, where for 2% chitosan/5% PG blended films onset temperature 253.3^{0}C. One stage degradation curve show, the onset temperature and 50% degradation temperature of 2%chitosan film is higher than that of 2% chitosan/5%PG blended films. Again this figure shows DTG of 2% chitosan and 2%chtitosan/ 5% PG blended films. There are three peaks in 2% chitosan and 2%chitosna /5% PG blended films.

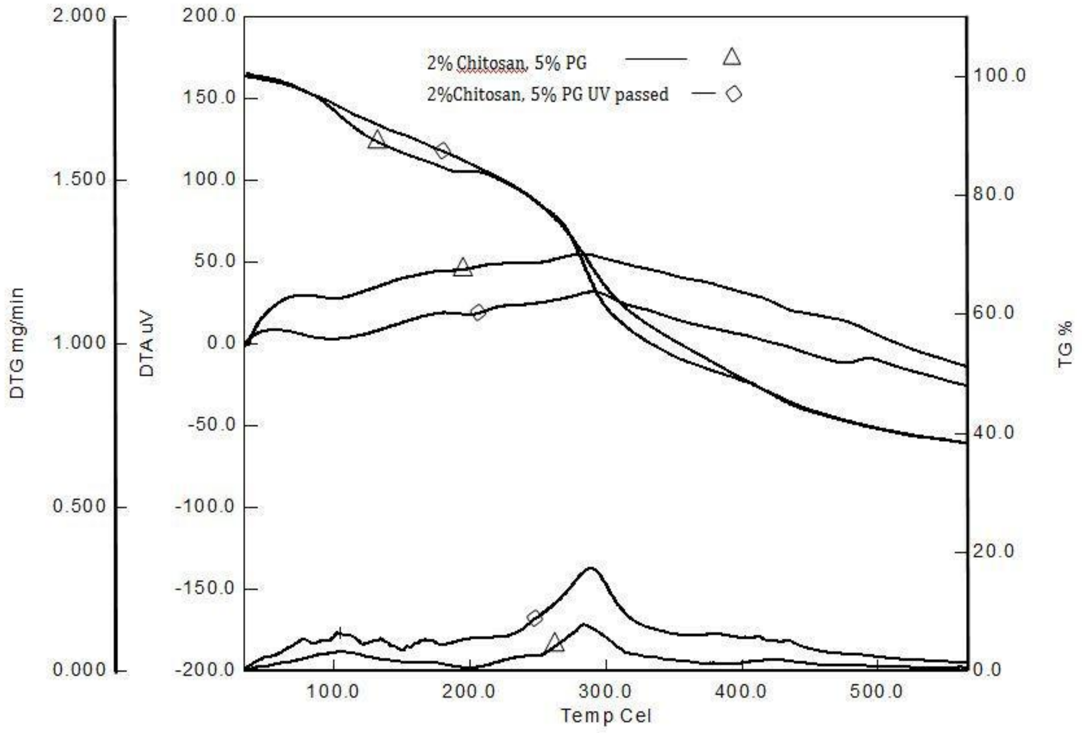

Figure 10: TG, DTA and DTG curves of 2% chitosan/5% phosphate glass blended film (untreated) & 2% chitosan/5% phosphate glass blended film (treated) with formulation F4 at 30th UV- passes (radiation doses).

Figure 10 shows that TG, DTA and DTG curve of 2% chitosan/5% PG blended films (treated) with formulation F4 at 30th UV-passes. The curve shows an initial 9.5% loss correspond moisture content. Four endothermic DTA peaks were observed at 97.6^{0}C, 199.1^{0}C, 254.3^{0}C and 474.4^{0}C respectively, however one exothermic peak was observed at 289.2^{0}C. The 1st at 97.6^{0}C is due to removal of moisture, 2nd peak is for lighter material, 3rd peak for heavier material, 5th peak for degradation and 4th peak due to heat evolved. Two DTG peaks were also found at 104.5^{0}C and 288.1^{0}C, which are, correspond to lighter material and heavier material. DTG curve depicts that the maximum degradation occurs at the temperature 288.1^{0}C with the rate of 0.314 mg/min.

Table 4: DTA of 2% chitosan, 2% chitosan/5% phosphate glass blended (untreated) film and 2% chitosan/5% phosphate glass blended (treated) film

Sample	1st peak	2nd peak	3rd peak	4th peak	5th peak
2% Chitosan film	99.0 ^{0}C	183.7 ^{0}C	261.5 ^{0}C	286.8 ^{0}C	460.5 ^{0}C
2% Chitosan/5% phosphate glass blended film (untreated)	101.7 ^{0}C	194. ^{0}C	261.1 ^{0}C	284.9 ^{0}C	432.1 ^{0}C
2% Chitosan/5% phosphate glass blended film (treated)	97.6 ^{0}C	199.1 ^{0}C	254.3 ^{0}C	289.2 ^{0}C	474.4 ^{0}C

The thermal stability of 2% chitosan/5% PG blended film (treated) is better than that of 2%chitiosan/ 5%PG blended film (untreated). Here for 2% chitosan/5% PG blended film onset temperature 253.2 ^{0}C, where 2% chitosan/5% PG blended film (treated) onset temperature was 255.0 ^{0}C. The onset temperature and 50% degradation temperature of 2% chitosan/5% PG blended film (treated) is higher than that of 2% chitosan/5% PG blended film (untreated). DTG curve shows three peaks in 2% chitosan/5% PG blended film (untreated) and two peaks in 2% chitosan/5% PG blended film (treated). Table-4 and Table-5, shows a comparative studies of DTA and DTG analysis of 2% chitosan, 2%chitosan/5%phosphate glass blended(untreated) film and 2% chitosan/ 5% phosphate glass blended (treated) film.

Table 5: DTG of 2% chitosan, 2% chitosan/5% phosphate glass blended (untreated) film and 2% chitosan/ 5% phosphate glass blended (treated) film

Sample	Maximum at (^{0}C)	Degradation rate mg/min
2% Chitosan film	287.7	0.183
2% Chitosan/5% phosphate glass blended film (untreated)	284.9	0.141
2% Chitosan/5% phosphate glass blended film (treated)	288.1	0.314

FTIR Analysis

In the prepared miscible blended films, it is expected that the intermolecular hydrogen bonding between the hydroxyl groups and the NH groups of the fibroin might be created. In order to have a better understanding of the types of interactions between the blended polymers, FTIR spectra of all the prepared blend films were studied. Figure 11 represents the FTIR spectrum of Chitosan film. It was found that the C-O stretching band appeared at 1060 cm^{-1}, which is an indication of the presence of chitosan. The strong band corresponds –CONH- groups of chitosan appeared at 1639 cm^{-1}. There are several peaks corresponding to the groups found in chitosan, such as 827, 1274, 1458 and 1639cm^{-1}. The spectrum is suitable comparable to those of the published spectrum. This FT-IR suggests that chitosan was extracted successfully.

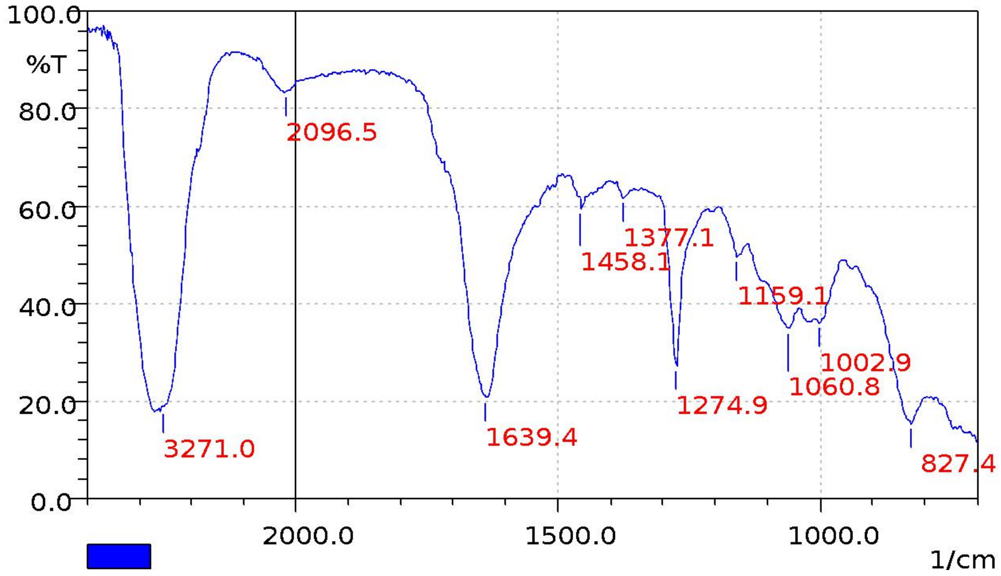

Figure11. FT-IR spectrum of chitosan

The FTIR spectrum of chitosan/phosphate glass blended film was obtained that showed a characteristic peak at 3246 cm^{-1} indicating the presence of broad O-H stretching band. The peak at 1055.48 cm^{-1} and 671 cm^{-1} corresponds to the C-N stretching (weak) band and N-H bending strong band respectively. Another FT-IR spectrum of chitosan/phosphate glass blended films (using 100% PEG in methanol at 30th UV-pass) was also done which showed a characteristic peak at 3471.66 cm^{-1} indicating the N-H stretching band due to the intermolecular hydrogen band between two polymers chitosan and PEG. This observed peak confirms strong blending of chitosan/ PG with cross linking-agent PEG.

Conclusion

The TS and Eb of the raw chitosan film are not satisfactory, as it was damaged in water. In this study, four different blends of various compositions were prepared by casting and mechanical properties were evaluated. 5% phosphate glass containing chitosan film performed the highest tensile strength (7.80 MPa)) and 1% phosphate glass containing chitosan film showed the highest elongation properties (107.7 %). The effect of UV radiation on the mechanical properties of chitosan, PG and their blend was investigated. From this investigation, it can be concluded that UV radiation is effective in improving the mechanical properties of chitosan, PG and their blend. A series of formulations was developed with PEG in methanol. The highest tensile strength is achieved with 100% PEG, 0% methanol using 2% photoinitiator at 3 minutes soaking time at 30th UV- pass in 5% phosphate glass containing chitosan film. The highest TS was 13.80 MPa. The highest polymer loading is achieved with 100% PEG, 0% methanol using 2% photoinitiator at 3 minutes soaking time at 20th UV- pass in 5% phosphate glass containing chitosan film. The highest elongation at break achieved with 50% PEG, 48% methanol using 2% photo initiator at 3 minutes soaking time at 10th UV-pass in 5% phosphate glass containing chitosan film. The highest Eb is 31.54%. The DTA/TG study also showed that 5% phosphate glass containing chitosan film (treated) was more thermally stable than that of untreated one. Onset temperature of 5% phosphate glass containing chitosan film (treated) was 255.0 ^{0}C; whereas the onset temperature for the untreated film was 253.2°C.

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