Fabrication and Thermo-Mechanical Characterization of HEMA Treated UV Photo-Cured Biodegradable Chitosan Film

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Abstract: Chitosan was extracted from dried prawn shell *via* chitin and was characterized by Fourier Transformed Infrared (FTIR) Spectroscopy. Thin film of chitosan was prepared by solution casting using a 2% chitosan solution. Chitosan was dissolved in 2% acetic acid. Mechanical properties like tensile strength (TS) and elongation at break (Eb%) of chitosan film were studied. Eight formulations (M1: 5% HEMA to M8: 40% HEMA) were developed with 2-hydroxyethyl methacrylate (HEMA) monomer in methanol (MeOH) along with photoinitiator Darocur-4043 (2%). The film was soaked in those formulations for 1 min and cured under UV radiation at different radiation intensities for the improvement of physico-mechanical properties of the film. The cured films were then subjected to various characterization tests like TS, Eb%, water absorption, FTIR spectroscopy, polymer loading (PL), differential thermal analysis (DTA), and thermo gravimetric analysis (TGA). The M6 formulation containing 30% HEMA in MeOH solution showed the best performance at 20th UV pass. The highest TS, Eb% and PL were found to be 31 MPa, 71.25% and 26.38%, respectively, for the same formulation at 20th UV pass. The DTA/TGA study showed that the film with M6 formulation at 20th UV pass was thermally more stable than non-radiated chitosan film. The FTIR analysis revealed the crosslinking between HEMA and chitosan.

Keywords: Chitosan, monomer, cross-linking, grafting, photo-cured, UV radiation.

1. INTRODUCTION

World is now going towards natural things. The natural polymer is biodegradable, easily decomposable and environmentally friendly [1]. The polymer materials that are biodegradable are now enjoying considerable popularity, especially from the standpoint of environmental protection [2]. The waste recycling processes are now promising research work. Bangladesh, being the largest delta country in the world, enjoys enriched prawn cultivation. Moreover, Bangladesh is a country of river. Here prawn is available in large quantities, containing highly natural polymer. There are 23,423 prawn farms in 25 districts of Bangladesh [3]. Satisfying local demand, a major part of the prawn is being exported to foreign countries. A large amount of prawn shell are thrown from many prawn processing areas and these thrown prawn shell remain unused and become waste, although these prawn shell waste retains highly natural polymer, thus creating environmental pollution. Chitin is obtained from these prawn shell wastes by deproteinization and demineralization operation [4]. Chitin, the second most abundant polymer in nature, is a linear polysaccharide composed of 2-acetamido-2-deoxy-D-glucosidic bonds. The principal derivative of chitin is chitosan, generally produced by alkaline deacetylation of chitin. Its primary structure corresponds to a linear chain of β-1-4 linked 2-amino-2-deoxy-D-glucopyranose residue [5, 6]. Chitin and chitosan has different fields of application and biodegradable in nature. In the different countries of the world, chitin and chitosan are also manufactured commercially in large scale from the outer shell of crustaceans (shrimp and crab). Chitosan is being used in many traditional and potential applications like in water and beverages clarification and purification [7], wound dressings, drug delivery, contact lens, bandages, cholesterol reducing agent, cosmetic and personal care etc. [8, 9]. A lot of research works has done using chitosan on different fields [10-19]. Few works in the electrical area using the biopolymer chitosan have been noticed [20]. From literature studies, several works were done on chitosan films. Chitosan film bears relatively better physical and mechanical properties. But its durability and stability in water is not satisfactory. Photo-curing is an active method for the development of chitosan application, especially in the field of chitosan films and its bio-blends. The field of photo-curing has been developed to an important branch of photo cross-linking of polymers [14]. Photo cross-linkable polymers possess functional groups which can undergo radiation-induced reactions to form a cross-linked polymer directly. This means that light irradiation of polymers carrying more

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E-ISSN: 1929-5995/14

than two reactive groups per chain (or of blend with a photoinitiator or photo-sensitizer) initiates cross-linking to a three dimensional network structure [21]. The present investigation deals with preparation and characterization of chitin and chitosan, extracted from prawn shell waste. Multifunctional vinyl unsaturated monomer was used in the treatment of chitosan polymeric films and its bio-blends, to reduce the UV radiation intensities to obtain optimum properties or to achieve an increased state of cure at the same time UV radiation intensities. In this respect, HEMA was used as tri-functional monomer which gives the films character more hard and brittle. To avoid these difficulties, a mono-functional monomer MeOH was mixed with HEMA at different proportion, which leads to the polymers softer and imparts some flexibility. HEMA is more effective in producing denser network than MeOH [22]. These films were treated with HEMA monomer along with MeOH and cured under UV radiation at different intensities. The treatment of monomer as well as radiation intensities was investigated through the enhanced mechanical and thermal properties of the films [24-26]. The objective of this study was to prepare chitosan and its film and then to investigate the effect of UV radiation on the thermo-mechanical improvement of the film in presence of HEMA monomer.

2. EXPERIMENTAL

2.1. MATERIALS

Chitosan was prepared in our laboratory from waste prawn shell and the extraction method was mentioned elsewhere in this paper.

2.2. Chemicals and Reagents

Clear liquid HEMA (molecular weight: 130.14, melting point: -12 ^{0}C, boiling point: 205 ^{0}C, miscible in water) was purchased from Fluka Chemie AGCH-9470 Buchs. MeOH and Photo-initiator Darocur-4043 (molecular formula: $C_{10}H_{12}O_2$, molecular weight: 164.204 g/mol) were procured from E Merck, Germany. Reagent grade acetone (CH_3-CO-CH_3), acetic acid (CH_3COOH) and hydrochloric acid (HCl) were supplied by BDH Chemicals Limited, England. Sodium hydroxide pellets (NaOH) was purchased from Merck Specialities Private Limited, India.

2.3. Extraction of Chitosan

The collected waste prawn shell was washed with hot water and dried in an oven at 105 °C for 72 hours. Dried prawn shell was pulverized using blender. Ground prawn shell was deproteinized with 1 N NaOH solution at boiling temperature for 4 hours (prawn shell: NaOH = 1:16, w/v) and demineralinzed with 1 N HCl solution at boiling temperature for 4 hours (Chitin:HCl = 1:13, w/v). The mixture was then washed with distilled water, filtered to neutralize and dried at 105 °C in an oven for 24 hours. Thus, prepared chitin is an intermediate product of chitosan. Chitosan was obtained by deacetylation of chitin using NaOH (Chitin: NaOH = 1:20, w/w) at 100 °C for 3.5 hours [5]. After this process, solid was separated from the alkali and was extensively washed with distilled water to remove traces of alkali. The resultant solid was dried in a vacuum oven at 50 °C for 24 hours. Chitosan was extracted in this way from prawn shell waste.

2.4. Preparation of Chitosan Films

Accurately weighed 2 gm chitosan (weighed on a Mettler AE 160 balance with reproducibility 0.01 mg, made in USA) was dissolved in 100 ml aqueous acetic acid (2%) solution in room temperature with constant stirring. The fully dissolved solution was then cast on to the silicon paper covered glass plate to form film. The solution layer was maintained into a thickness of 0.10 mm on the glass plate. The solution was dried into films at room temperature for 48 hours. The dried films were then peeled from the silicon cloth and cut into small pieces of length 70 mm and width 10 mm. These samples were stored in laminated polythene bag and kept in desiccators at room temperature prior testing.

2.5. Soaking of the Chitosan Films in HEMA Solution

Different percentages (5-40% by wt.) of HEMA solution were prepared containing 2% photoinitiator in MeOH (93-58 % by wt.). Eight formulations, named M1-M8, were prepared and the compositions were given in Table **1**. The chitosan films were soaked in these solutions for 1 min prior to UV-curing.

2.6. Curing of the HEMA Soaked Chitosan Films Using UV Radiation

To cure the HEMA soaked chitosan films, an UV irradiator, Minicure-200 UV lamp, (IST Technik, Germany) was used. The intensity of the lamp was 2 kW at 9.5 Amp current. The wave length of the UV was 254-313 nm. The samples were run under the UV lamp at a speed of 4 m/min or 8 passes/min with the help of a conveyor belt interlocked with the machine. The Minicure-200 has the efficiency within ±1%. The films

Table 1: Composition of Different Monomer Formulations (%w/w)

Formulations	MeOH (%)	HEMA (%)	Photoinitiator (%)
M1	93	5	2
M2	88	10	2
M3	83	15	2
M4	78	20	2
M5	73	25	2
M6	68	30	2
M7	63	35	2
M8	58	40	2

were exposed at room temperature for 24 hours for better grafting.

2.7. Characterization of the Radiated and Non-Radiated Films

The Films were exposed at room temperature for well grafting about 24 hours. After this, TS, Eb%, PL, DTA/TGA/DTG, FTIR and water uptake were measured. The experimental flow diagram was presented in the Figure **1**.

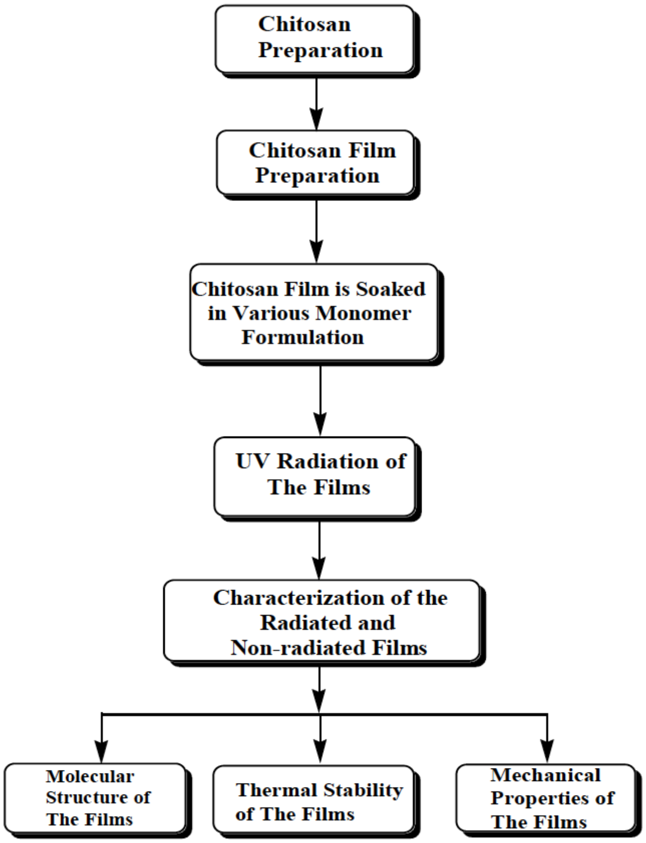

Figure 1: Experimental flow diagram.

2.8. Mechanical Properties

TS and Eb % of treated and untreated chitosan films were measured using Universal Testing Machine (INSTRON, model 1011, UK). The load capacity was 500 N, efficiency is within ±1 %. The crosshead speed was 10 mm/min. Gauze length was 20 mm. Following equations are used to measure the mechanical properties.

$$\text{Tensile strength, TS (MPa)} = \frac{\text{Load (N)}}{\text{Thickness (mm) x Width (mm)}}$$

$$\text{Elongation at break, Eb (\%)} = \frac{\text{Displacement at break}}{\text{Gauze length}} \times 100$$

2.9. Polymer Loading

The polymer loading of the films was determined on the basis of weight gained by the films after the entire treatment process. Polymer loading is determined by the following equation.

Polymer Loading, PL (%) = $[(Wt - Wo) / Wo] \times 100$

Where, Wt = Weight of the treated dry sample and Wo = Weight of the dry sample before treatment.

2.10. Water Uptake

The water uptake of the radiated and non-radiated films was periodically monitored up to 5 minutes to find the water uptake feature of the films. Water uptake is determined using the following equation.

$$Wg = \frac{(Wa - Wo)}{Wo} \times 100$$

Where, Wg = % of weight gained by the sample due to water absorption, Wa = Weight of the sample after

Table 2: **Tensile Properties of Chitosan Film**

Material	Tensile Strength (MPa)	Elongation at break (%)
Chitosan Film	24	38

water treatment and Wo = Weight of the dry sample before water treatment.

2.11. Thermal Analysis (DTA/TGA/DTG)

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.

2.12. Fourier Transformed Infrared Spectroscopy Analysis

The FTIR spectroscopy of radiated and non-radiated chitosan films were performed by ATR-FTIR Spectrophotometer (Paragon 500-Model, Perkin Elmer, Beaconsfield, Buckinghamshire, UK) in the wave number range 400–4000 cm^{-1} with resolution of 4 cm^{-1}. The FTIR spectrum was taken in a transmittance mode. A hollow hard paper was made and the film (2cm×7cm) was attached at the hollow place of the paper. Then the films were characterized by FTIR spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties and Water Uptake of Non-Radiated Pure Chitosan Films

Mechanical properties (TS and Eb%) of the virgin chitosan film were measured after 1 day of the film formation and the values were represented in the Table **2**. TS value was found 24 MPa and Eb% was found 38%. The water uptke profile of the pure chitosan film against soaking time was plotted in the Figure **2**. From the Figure **2**, it is clear that; chitosan absorbed water gradually with time and attained a plateau after 4 min. The water absorption of the pure chitosan film was initially rapid. The film absorbed 194% of water after 1 min, while as, it absorbed 287% after 2 min. The water absorption was saturated at 520% after 4 min. This higher amount of water uptake of the pure chitosan film

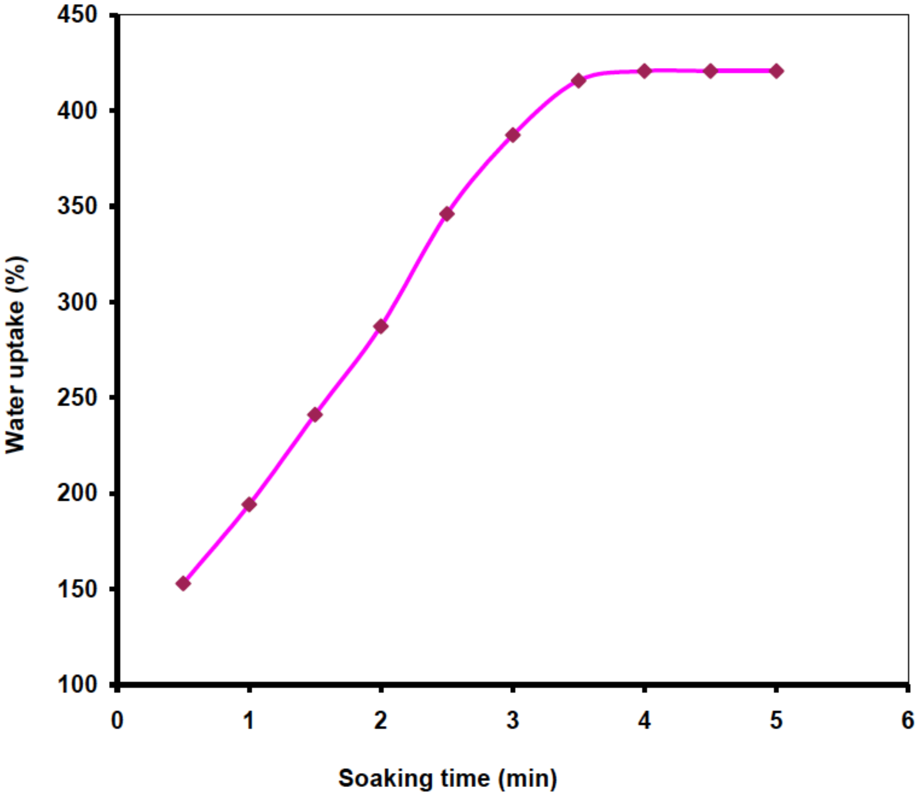

Figure 2: Percentage water uptake of pure chitosan film against soaking time (min).

is due to the presence of –OH groups in its structure [24, 25].

3.2. UV-Cured HEMA Soaked Chitosan Films: Optimization of Different Conditions

3.2.1. Optimization of Monomer Formulation

The chitosan films were soaked in different formulations (M1 to M8) for 1 min. After soaking, the films were cured under UV radiation at different intensities (5, 10, 15, 20, 25 and 30 pass). The samples were then subjected to different characterization tests after 24 hours of radiation to find an optimum formulation.

3.2.2. Polymer Loading of the HEMA Soaked UV-Cured Film

Monomer concentration plays an important role because it affects the polymerization rate and the over all conversion as well as the properties of the cross linked polymerization [1]. The result of PL values of the cured films against the total number of UV- radiation passes as a function of monomer formulation are presented in the Figure **3**. The highest PL was found 26.38% with the treatment of monomer concentration M6, containing 30% HEMA, 68% MeOH and 2% photoinitiator at 20th UV pass. PL value was increased with the total number of UV–radiation doses and attained a maximum value and then decreased. In all cases, the maximum PL value was obtained at 20th UV pass. Beyond 20th pass, the PL values were decreased. This may be due to the radiation degradation of the films at higher UV-pass [23, 24]. PL values were increased up to 30% HEMA (M6). But, above 30% HEMA decreased the PL values of the chitosan film. At low monomer concentration, vinyl monomer like HEMA promotes reaction with the help of photoinitiator leading to network polymer structure through curing *via* their double bonds. As the increase of HEMA concentration, the amount of residual instaurations is also increased with the consequence of faster rate of formation of three dimensional networks causing restricted mobility [25]. Homo polymerization dominates over monomer–chitosan backbone reaction at higher monomer concentration and this is the reason behind the decreased PL values of the films at higher HEMA concentration [25].

3.2.3. Tensile Strength of the HEMA Soaked UV-Cured Film

Tensile strength is very important in selecting diverse application of polymer. The results of TS values were shown in the Figure **4**, where TS values were plotted against the number of UV pass as a function of monomer formulations. With the HEMA treatment, the TS values of the treated chitosan film were increased. This increased of TS is due to the cross- linking of the hydroxyl and amino group in chitosan with vinyl group forming three dimensional network structures. From the Figure **4**, the highest TS value of 31 MPa was achieved with the monomer M6 formulation at 20th UV pass. The presence of hydroxyl and amino group of chitosan film

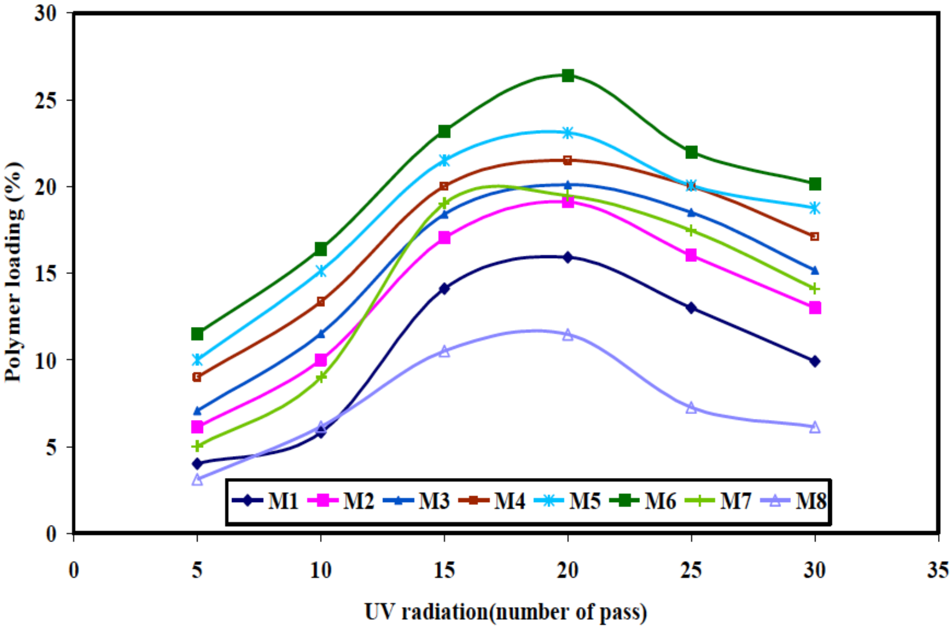

Figure 3: Polymer loading (PL) of the treated chitosan film against UV radiation (number of passes) with respect to different monomer formulations.

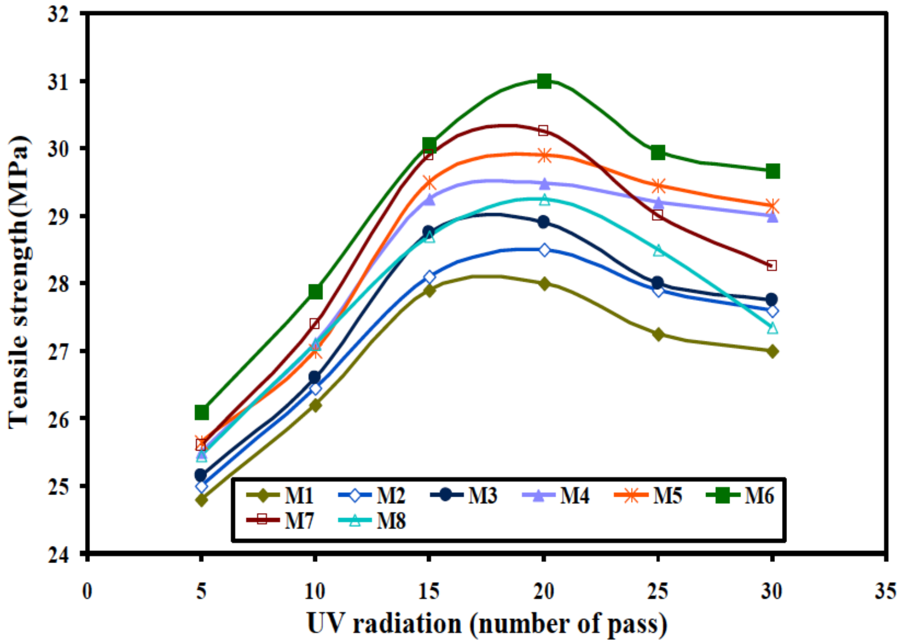

Figure 4: Tensile strength (TS) of the treated chitosan film against UV radiation (number of passes) with respect to different monomer formulations.

may be allowed for photo-curing reaction with HEMA. Above 30% HEMA concentration, the TS values were decreased. For instance, the TS values were found 30 MPa and 29 MPa, respectively for M7 and M8 formulation at 20th UV pass. This may be due to the fact that the formation of homo-polymer between HEMA-HEMA is dominant and the reaction of chitosan film with HEMA is less prominent [25]. For all formulations, the TS values were increased up to 20th UV pass but beyond it they were decreased. This may be due to the degradation of polymer chain at higher radiation doses and the film became hard, twisted and brittle [26].

3.2.4. Elongation at Break of the HEMA Soaked UV-Cured Film

The elongation property at the break is related to the elastic and brittle character of the film. HEMA gives

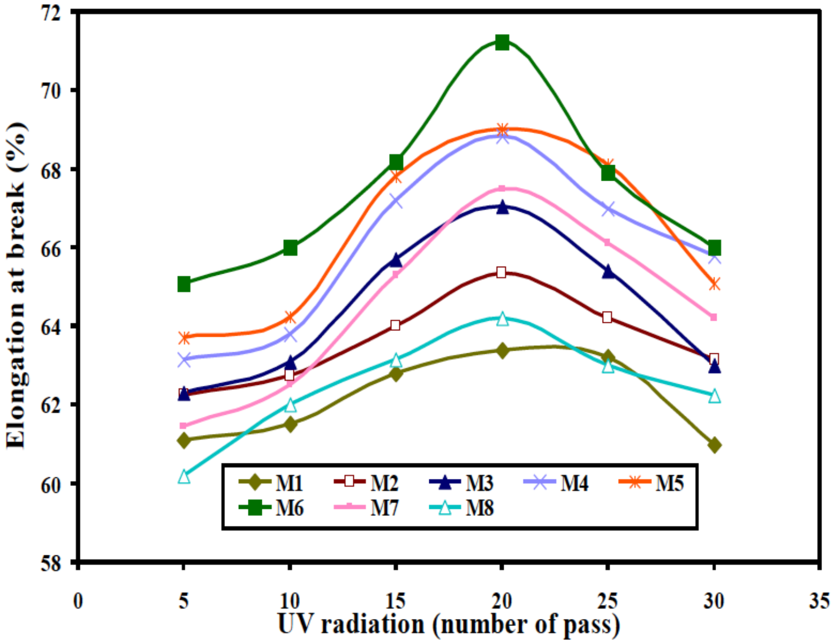

Figure 5: Elongation at break (Eb%) of the treated chitosan film against UV radiation (number of passes) with respect to different monomer formulations.

higher Eb% with UV-radiation doses. This is due to its inherent character for higher elastic property. The results of Eb% were plotted in Figure **5** against the total number of UV pass as a function of monomer formulations. From the Figure **5**, the maximum Eb% was obtained 71.25% for M6 formulation at 20th pass of UV radiation. There was a rise in elongation at the initial pass of UV radiation. The Eb% was increased with the number of UV pass and after attaining maximum value at 20th UV pass, Eb% was decreased. The formulation M6 treated film which provided the highest TS; also showed the highest Eb%. HEMA increases high elasticity and imparts flexibility [22]. So, it is clear that TS and Eb% are very much dependent on the nature of the formulation [25], where the monomer is monofunctional or multifunctinal. The combination of HEMA and MeOH at the ratio of 30 and 68% respectively (M6), yields the suitable condition for the best cross- linking phenomenon at the equilibrium condition that creates the chitosan film with the highest TS and highest Eb%. The treatment of monomer and UV radiation intensities with mechanical properties were reported [10, 12, 23-26].

3.3. Percentage Water Uptake Versus UV-Pass of the Optimized Film

The cured chitosan films were soaked in water contained in a static bath at 25 °C for 5 minutes. Percentage of water uptake of the optimized chitosan film (M6) was plotted with varying UV-radiation doses (number of pass) against immersion time (min) in Figure **6**. From the Figure **6**, it was observed that water uptake of all samples during first few times was faster and then it slowed down and eventually attained plateau. Water uptake of the radiated chitosan film remained almost constant after immersing for 3 minutes. The water content absorbed at the saturated level (at plateau region) is regarded as the equilibrium water uptake. The maximum water uptake was found for 5th UV pass sample but 20th UV pass showed the minimum. For 1 min of immersion time, the maximum value of water uptake was 50% for 5th UV pass while the minimum value was 25.1% for 20th UV pass. It was figured out from the Figure **6** that, there was a substantial water absorption reduction of the HEMA treated chitosan film. Water absorbency (at equilibrium) was decreased with the increase in PL. The most reduced water uptake at maximum PL is due to the maximum cross-linking of the hydroxyl and amino group of the chitosan with vinyl group of the HEMA, forming three dimensional network structures, remaining least free vacant space at polymer chain for water absorption [25].

3.4. Thermal Stability Analysis of the Pure and Treated Chitosan Film

The TGA, DTA and DTG curves of non-radiated pure chitosan (2%) film were shown in the Figure **7**. The TGA curve showed an initial 12.6% loss corresponds to moisture content. Then the mass was continuous losing having initial slower rate and the ending was faster rate. The lighter substances removed initially and then heavier material removed. 50% loss is 66.6% took place at 288.5 °C. Four endothermic DTA peaks were observed at 99.0 °C,

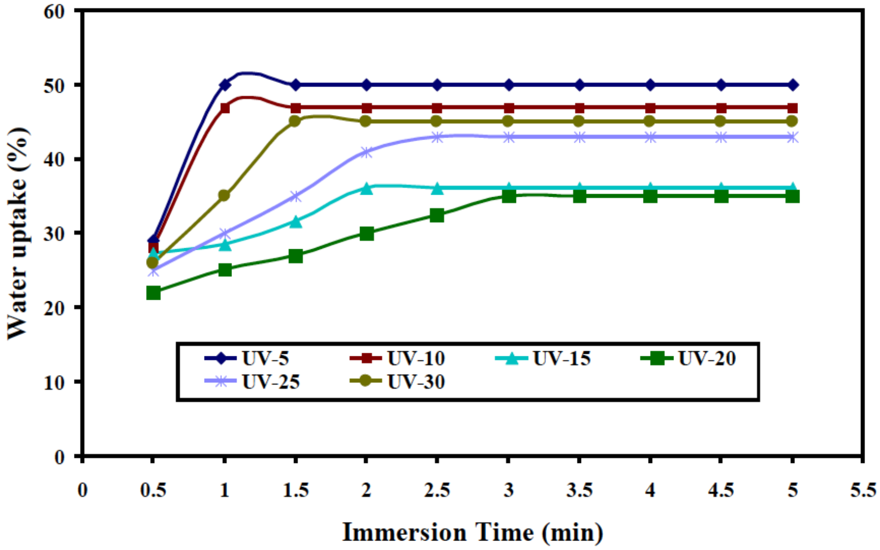

Figure 6: Percentage water uptake of optimized (M6 formulation) chitosan film against immersion time as a function of different UV passes.

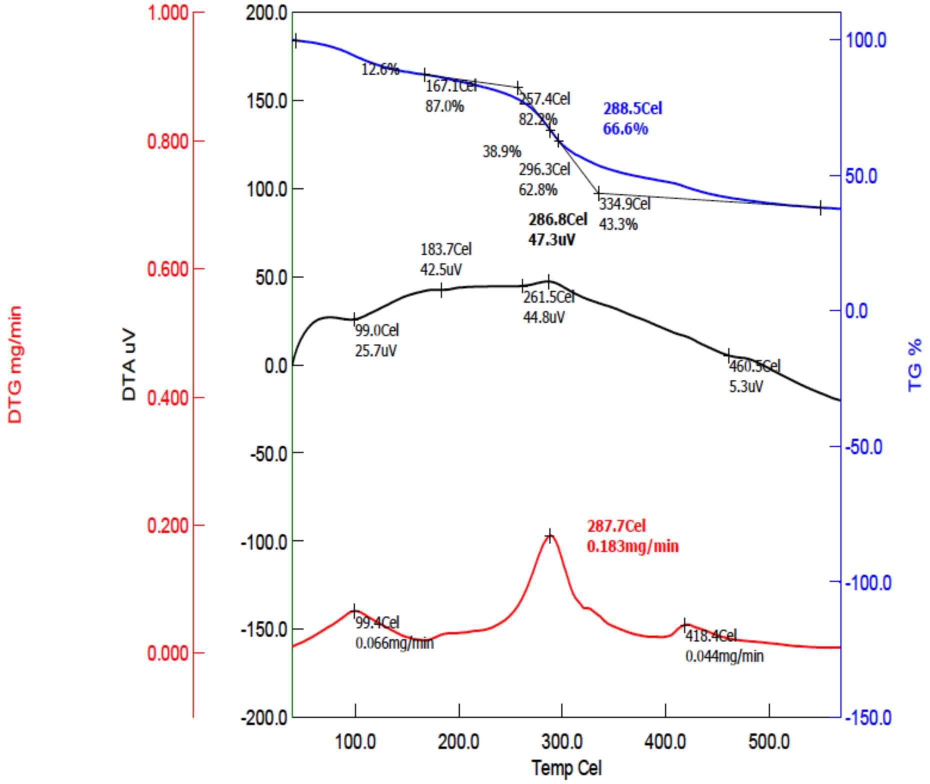

Figure 7: TGA/DTA/DTG curves of non-radiated 2% chitosan film.

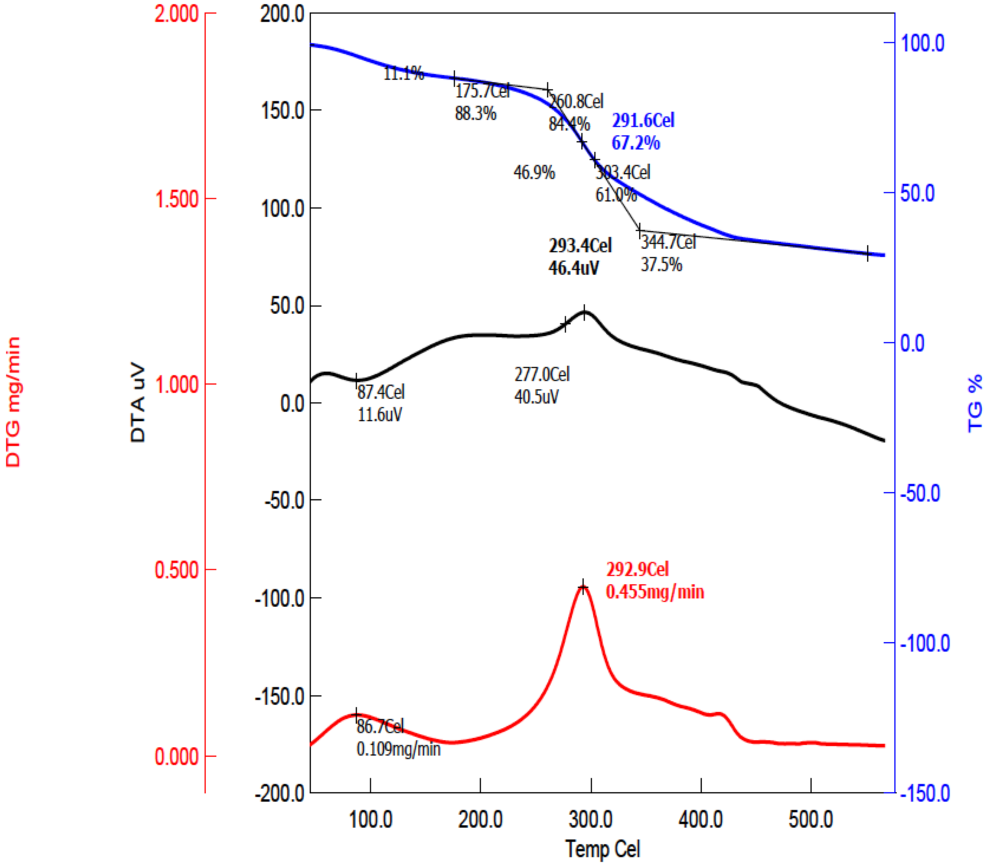

Figure 8: TGA/DTA/DTG curves of UV radiated M6 formulation film at 20th UV pass.

183.7 °C, 261.5 °C and 460.5 °C respectively but exothermic peak was observed at 286.8 °C. The 1st peak at 99.0° C was due to removal of moisture, 2nd peak was for lighter material, 3rd peak for heavier material, 4th peak for heat evolved and 5th peak for degradation. Three DTG peaks were also found at 99.4 °C, 287.7 °C and 418.4 °C which were correspond to lighter material and heavier material. DTG curve of pure chitosan film depicted that the maximum degradation occurs at the temperature 287.7 °C with the rate of 0.183 mg/min.

3.5. Fourier Transformed Infrared Spectroscopy (FTIR) Analysis

FTIR is of importance to study the molecular structure. FTIR analysis was carried out using Perkin Elmer FTIR Spectroscopy. For this purpose, pellet of chitosan was made with solid KBr. The IR range was taken from 400-4000 cm^{-1}. The FTIR spectrum of radiated film was different from that of the pure non-radiated polymer. Figures **9** and **10** showed the infrared spectra for the pure non-radiated chitosan and radiated

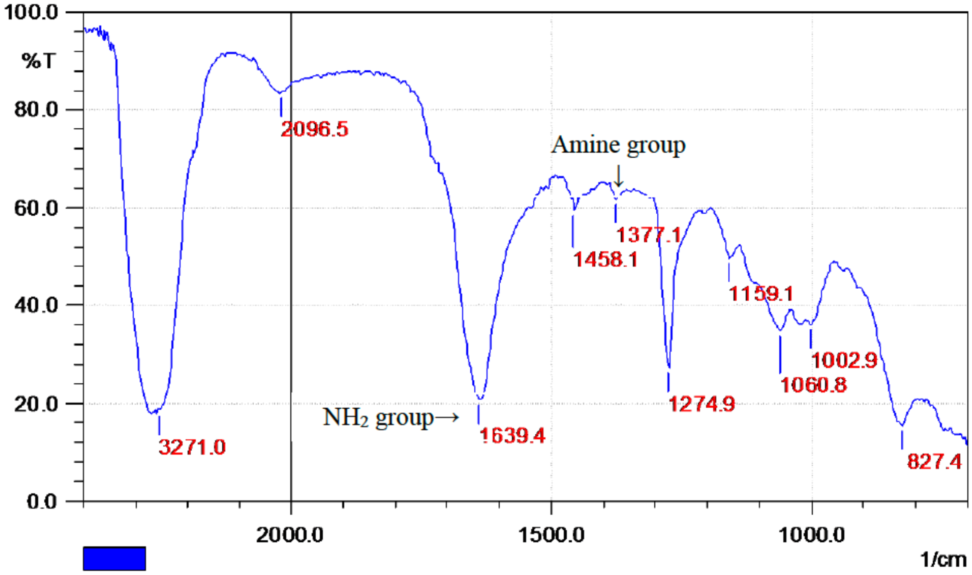

Figure 9: FTIR spectra of neat chitosan film.

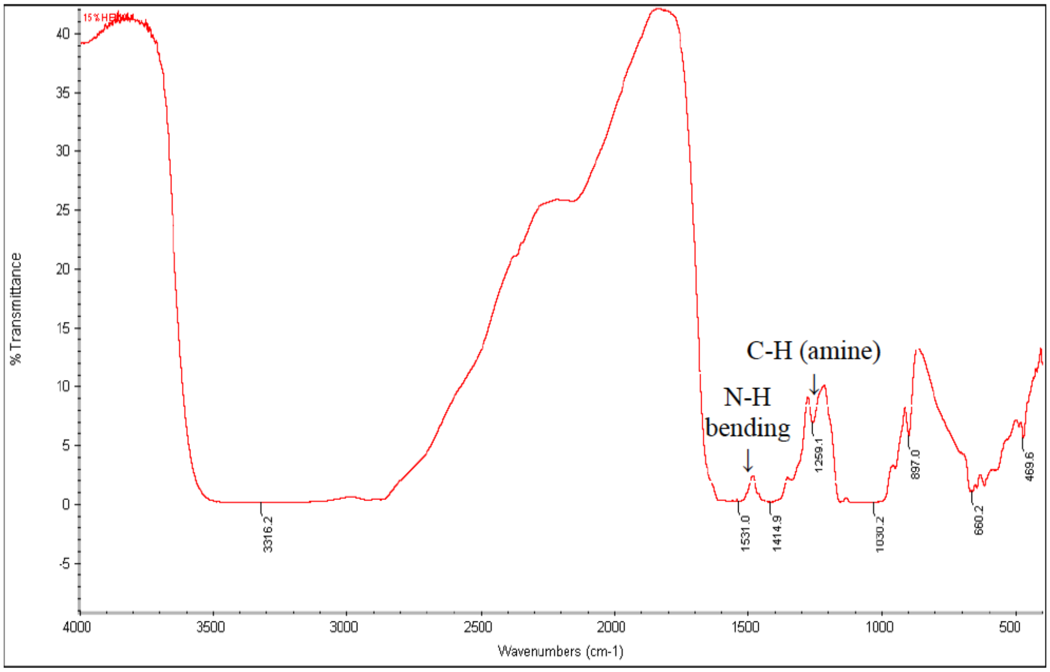

Figure 10: FTIR spectra of chitosan treated with HEMA monomer followed by UV radiation treatment (M6 formulation).

M6 formulation, respectively. It was found from the Figure **9** that the C-O stretching band appeared at 1060.8 cm^{-1} which is indication of the presence of chitosan. The strong band corresponds NH_2 groups of chitosan appeared at 1639.4 cm^{-1}. Again, bands of C-H bond (stretching), O-H bond, C-N (amine) bond and C-H (CH_2 bending) bond were appeared at 2096.5 cm^{-1}, 3271 cm^{-1}, 1377.1 cm^{-1} and 1458.1 cm^{-1}, respectively. This FTIR suggested that chitosan was extracted successfully. Again from FTIR analysis of M6 formulation, we observed that O-H band was appeared at 3316.2 cm^{-1} and band of N-H bending was appeared at 1531 cm^{-1}. Similarly, bands of C-N (amine) bond, C-O bond and C-H (CH_3 bending) bonds were appeared at 1259.1 cm^{-1}, 1030.2 cm^{-1} and 1414.9 cm^{-1}, respectively. There was no band for C=C bond. This was due to the crosslinking between monomer and polymer. Important peaks are labelled in the figures.

CONCLUSION

Chitosan was extracted from prawn shell through the formation of chitin and was characterized by FTIR. Chitosan films were prepared using HEMA and MeOH along with photoinitiator. The films were cured under UV radiation. The prepared films were investigated. The highest polymer loading (26.38%), tensile strength (31 MPa) and elongation at break (71.25%) were achieved for the film prepared with M6 formulation containing 30% HEMA monomer at 20th UV pass. The HEMA soaked UV irradiated chitosan films showed lower water absorption ability. The DTA/TGA study showed that M6 formulation cured at 20th UV pass was more thermally stable than their counter part non-radiated chitosan film. This study revealed that the thermo-mechanical properties of chitosan films improved using acrylic monomer and UV radiation by keeping the inherent properties of chitosan.

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Received on 17-03-2014 Accepted on 10-05-2014 Published on 25-06-2014

DOI: http://dx.doi.org/10.6000/1929-5995.2014.03.02.3