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Modification and Characterization of Chitosan Films Using 3-trimethoxyl Silyl Propylmethacrylate

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The biodegradable flexible chitosan film was prepared by solution casting. The physico-mechanical properties, polymer loading (PL), gel content and water uptake of the chitosan film were studied. The tensile strength (TS) and % elongation at break (Eb) of the uncured chitosan film were 7.0 (MPa) and 8%, respectively. Four formulations were developed using 3-trimethoxyl silyl propylmethacrylate (TSPMA) (varied from 10–80% by weight) in methanol along with photoinitator (Darocur-1664). The raw chitosan films were then soaked in the prepared formulations and cured under UV radiation at different intensities to improve the physico-mechanical properties of the films. TS for the photocured chitosan film was 28.0 (MPa) which was 4 times higher compared to the uncured chitosan film. This TS was obtained for the formulation containing 30% silane (TSPMA) at 24th UV pass for 4 min soaking time. The maximum PL of 45.1% was obtained for the same formulation at 24th UV pass for 4 min soaking time. The water uptake and gel content of the photocured chitosan films were also studied. The scanning electron micrographs of the photocured chitosan film showed smooth surface, compact and homogeneous structure.

Keywords: Chitosan, silane monomer, mechanical properties, UV-radiation

1 Introduction

Chitosan is a linear polysaccharide prepared by the alkaline or enzymatic N-deacetylation of chitin which is found in the outer shells of crabs, prawn, shrimp, lobsters, etc. Chitosan is an aminopolysaccharide, comprises unbranched chain of β (1 → 4)2-amino-2-deoxy-D-glucan residue (1–3). Chitosan is largely studied in pharmaceutical and medical fields for its biodegradability, biocompatibility, bioactivity and its interesting physicochemical properties. Chitosan is water soluble as the salts of various acids present in D-glucosamino unit (4–6). Partially acetylated chitosan that has about 50% D-glucosamine unit is only able to dissolve in water. These biopolymers are biorenewable, biodegradable and biofunctional (7–9). A great deal of research has been done using chitosan in different fields (10–15). The presence of active groups in chitosan molecules allows easy chemical modification. This is why chitosan is used in many fields and is well-known in the wound management application for its haemostatic properties. Biological properties of chitosan-like bacteriostatic and fungistatic properties are mainly useful for wound treatment. Chitosan films and membranes are used in dialysis, contact lenses, dressings and the encapsulation of mammal cells, including cell cultures. Chitosan sponges are used in dressings and to stop bleeding of mucous membranes. Chitosan fibers are used as resorbable sutures, non-wovens for dressings, and as drug carriers in the form of hollow fibers (8, 14-15). Research has been also carried out to use composites made of chitin nanofibrils and chitosan glycolate as wound medicaments (16). Its good miscibility with other polymers means that complexes and chelates are readily formed. The UV-curable chitosan derivatives were successfully used as coating materials for electro-less plating on non-conductive substances (17).

Monomeric silicon chemicals are known as silanes. This belongs to a class of organosilane compounds having at least two reactive groups. It works at an interface between an inorganic substrate (such as glass, metal or mineral) and an organic material (such as an organic polymer, coating or adhesive) to bond, or couple, the two dissimilar materials. The organofunctional portion of the silane can react, and bond to the polymer backbone. These versatile materials are used as promoters, dispersing agents, crosslinking agents, surface modifiers etc. As a crosslinking agent, it is used in various polymers like polyethers, polyurethanes,

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polyesters, etc. to improve the properties such as tear resistance, elongation at break, abrasion resistance, etc. A silane coupling agent can be made to be compatible with almost every type of organic polymer, thermosetting resins through elastomers. It may be applied to the substrate as a pretreatment (18). It has the ability to improve adhesion between organic and inorganic phases (19).

The present study deals with the preparation and characterization of thin films of chitosan. The ultimate goal was to observe the effect of the silane monomer named

3-trimethoxyl silyl propylmethacrylate (TSPMA) on the physico-mechanical properties of the chitosan films using a photocuring technique.

2 Experimental

2.1 Materials

Prawn shell was collected from Mongla (near the Sundarban forest) in Bangladesh. Sodium hydroxide (NaOH), ethanoic acid, 3-trimethoxyl silyl propylmethacrylate, photoinitiator (Darocur-1664) and methanol were supplied by Merck (Germany). Hydrochloric acid (HCl) was supplied by BDH (UK).

2.2 Method

2.2.1. *Extraction of chitosan from prawn shell*

Waste prawn shell was washed with hot water and dried in an oven at 105°C for 72 h. Dried prawn shell was ground and then deproteinized with 1 N NaOH solution at boiling temperature for 4 h (prawn shell: NaOH = 1:16, w/v) and demineralized with 1 N HCl solution at boiling temperature for 4 h (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 h. 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 h. After this process, the solid was separated from the alkali and extensively washed with distilled water to remove traces of alkali. The resultant solid was dried in a vacuum oven at 50°C for 24 h. Finally, chitosan was extracted from waste prawn shell.

2.2.2. *Preparation of chitosan film*

Table 1. Composition (% w/w) of soaking formulations containing silane monomer

	Monomer Compositions		*Photoinitiator*
Formulations	*Silane (%)*	*Methanol (%)*	*Darocur-1664(%)*
S-1	10	86	4
S-2	30	66	4
S-3	60	36	4
S-4	80	16	4

A solution of chitosan (2 g) was prepared in aqueous ethanoic acid (2%). Thin films of chitosan were prepared by casting the chitosan solution on silicon cloth (release film) mounted on a flat glass plate and film thickness was 0.10± 0.01mm. Four formulations were prepared in methanol using silane monomer in presence of photoinitator (2%). In the formulation % of silane was 10, 30, 60 and 80 and presented as S-1, S-2, S-3 and S-4 respectively in Table 1. Chitosan films were soaked in above formulations for 1-5 min and then irradiated under UV radiation at different intensities using a UV minicure machine (1ST Technik, Germany). The intensity refers to the number of UV- radiation pass. The intensity of the lamp was 2 kW at 9.5 amp current and the conveyor speed was 4 m/min. The wave length of UV was 254-313 nm.

2.2.3. *Characterization of the film*

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 2 mm/min and 20 mm, respectively with a load range 500 N. The gel content of the cured films was obtained by extracting a known weight of the film with hot benzene in a soxhlet for 48 h. The difference of weight of the film before and after the extraction process determined gel content. The polymer loading of the films of different monomer formulations was determined on the basis of weight gain by the film after the entire treatment process. Polymer loading, PL was determined by the following equation.

$$\mathrm{PL}\ (\%) = (\mathrm{W_t} - \mathrm{W_o})/\,W_o \times 100.$$

Where, $\mathrm{W_t}$ is the weight of the treated (dry) film and W_o is the weight of the untreated (dry) film. Water uptake was measured by soaking the chitosan film in distilled water contained in a static beaker at 25°C for 28 min. The water uptake of the cured films was periodically monitored to find the profile of water uptake. The FTIR spectroscopy of chitosan films was performed by FTIR Spectrophotometer (Paragon 500 Model, Perkin-Elmer, Beaconsfield, Buckinghamshire, UK) in the wave number range 400–3500 cm^{-1} with a resolution of 4 cm^{-1}. The FTIR spectrum was taken in a transmittance mode. The morphological study of the chitosan film was done using a JEOL 6400 SEM at an accelerating voltage of 10 kV. The SEM specimens were sputter-coated with gold.

3 Results and Discussion

Data presented here are average values of at least five samples and the associated error is ± 1%. Thin film of chitosan was prepared by casting 2% chitosan solution mentioned

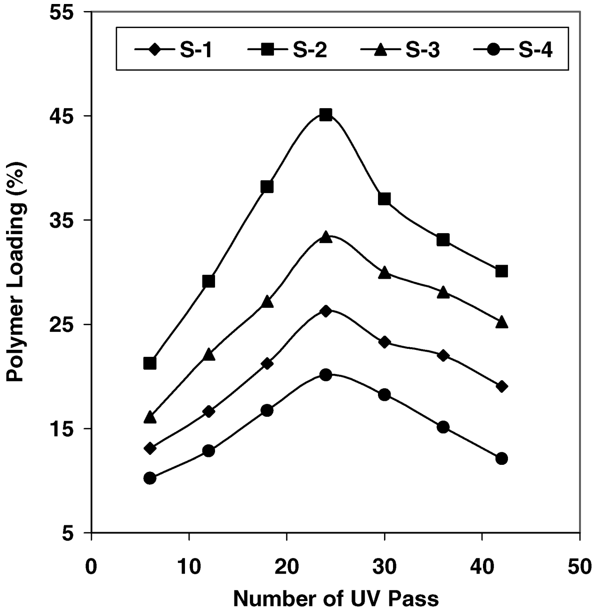


Fig. 1. Polymer loading of chitosan films against the number of UV passes with respect to the percentage TSPMA.

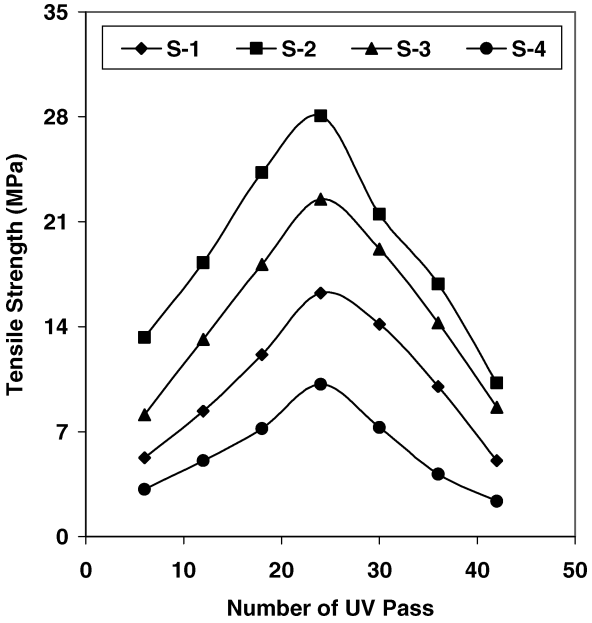


Fig. 2. Tensile strength of chitosan films against number of UV passes with respect to percentage of TSPMA.

earlier. Mechanical properties like TS and Eb were characterized. The TS and Eb of the raw chitosan films were 7.0 MPa and 8%, respectively.

3.1 Characterization of Chitosan Films

Chitosan films were soaked in monomer formulation (S-1 to S-4) for 1-5 min and irradiated under UV-radiation at different intensities (6, 12, 18, 24, 30, 36 and 42 passes). The cured films were subjected to various characterization tests after 24 h of UV radiation. Soaking the films in various percentages of monomer formulation was carried out to optimize a certain formulation on which the films would exhibit improved physico-mechanical properties. The PL values of the TSPMA treated chitosan films are plotted in Figure 1 against a number of UV passes as a function of TSPMA concentration for a 4 min soaking time. The PL values increased quite sharply at the initial irradiation and showed maximum PL value at the 24th UV pass for all formulations. Then, the increase of radiation intensities decreased the PL values for all cases and showed lower PL at the 42nd UV pass. This may be due to the radiation degradation of the films at higher UV passes (20). From Figure 1 it is clear that monomer formulation containing 30% TSPMA (S-2) showed the best result compared to other formulations. At 6, 12, 18, 24, 30, 36 and 42 passes the PL values were 21.2, 29.1, 38.2, 45.1, 37, 33.1 and 30.1%, respectively. The highest PL value was 45.1% which was about 71.6, 35 and 123.7% higher compared to S-1, S-3 and S-4 formulations, respectively. The lowest PL value is 30.1% for S-2 at 42^{nd} UV pass but still higher than other three formulations (S-1, S-3 and S-4). An increase of TSPMA concentration in the formulation decreased the PL values, which might be due to the dominating homo polymerization reaction between silane-silane radicals rather than the silane chitosan film reaction.

The results of TS values are represented in Figure 2 against the number of UV passes as a function of TSPMA concentration for a 4 min soaking time. From the figure it is observed that TS values increased with the increase of UV radiation intensities, as well as TSPMA concentration. The TS value reached the maximum at the 24th UV passes for S-2 formulation. The maximum tenacity was attained at 30% TSPMA and then the tenacity decreased as TSPMA concentration increased up to 80%. This indicated that the 30% TSPMA showed the most favorable condition for easy diffusion of the impregnating solution into the chitosan film backbone during equilibrium condition required for the polymerization process under the UV-radiation system. The highest TS value was 28 MPa at the 24th UV passes for S-2 formulation and about 4 times higher than that of raw chitosan film. Then, the TS values decreased with the increase of radiation intensities and showed 23.2, 39.8 and 63.3% lower TS at the 30, 36 and 42^{nd} UV passes, respectively, than that of highest TS value. Higher radiation intensities was responsible for the degradation of the films and hence the decrease of the TS values (9, 20). Concentration of TSPMA played a vital role on the enhancement of TS values. TS increased with the increase of TSPMA concentration and then decreased as the concentration increased in the formulation. The lowest TS is 2.3 MPa at the 42^{nd} UV pass for S-4 formulation containing 80% TSPMA. 35% TSPMA in the formulation showed the best result compared to other formulations.

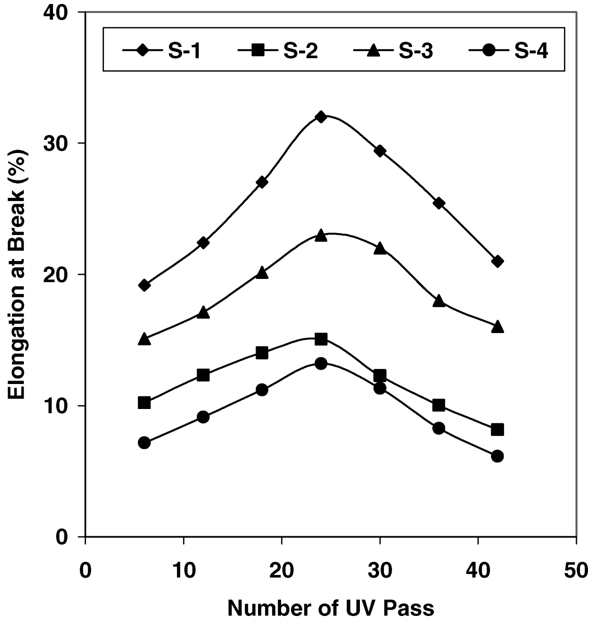


Fig. 3. Elongation at break of chitosan films against the number of UV passes with respect to the percentage of TSPMA.

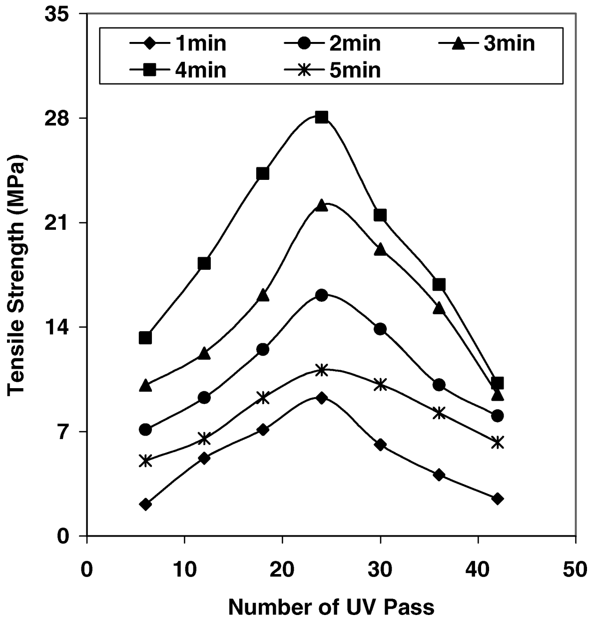


Fig. 5. Tensile strength of chitosan films against the number of UV passes with respect to soaking time.

Increasing the concentration of TSPMA decreased the TS values for various reasons, such as the films became brittle at higher TSPMA concentration and the rates of radical-radical combination and recombination reactions between them (radical) were also different from that of the optimum conditions that occur at 30% TSPMA concentration.

In Figure 3, % elongation at break of the TSPMA treated chitosan films are depicted against the number of UV radiation intensities for a 4 min. soaking time. From the figure it is observed that initially Eb increased with the increase of UV radiation dose. The highest Eb value was 32% obtained from S-1 formulation containing 10% TSPMA at the 24th UV pass. On the other hand, monomer formulation containing 30% TSPMA (S-2) showed the Eb value of 15% which was about 53.1% lower compared to highest Eb at S-1 and 87.5% higher than that of raw chitosan film.

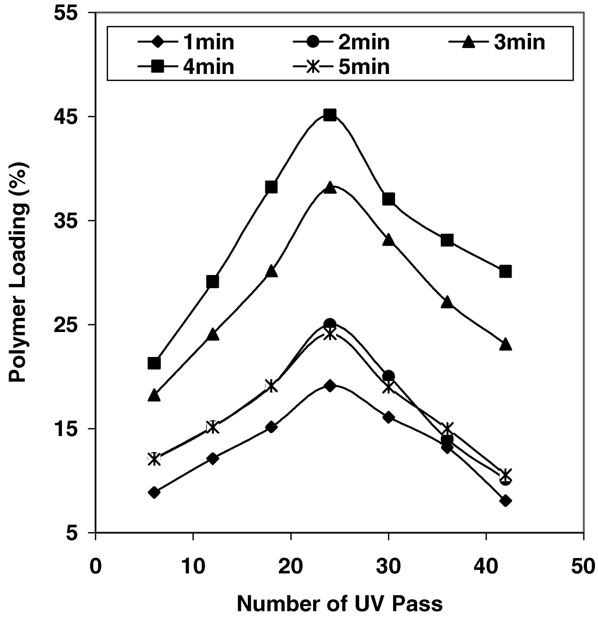


Fig. 4. Polymer loading of chitosan films against the number of UV passes with respect to soaking time.

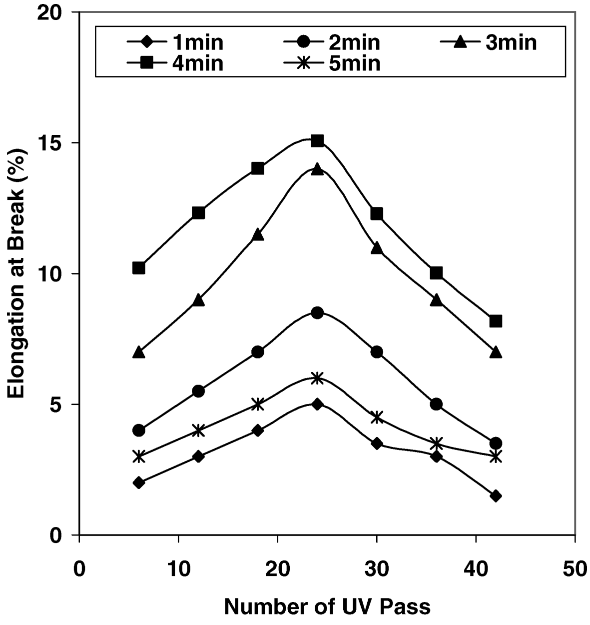


Fig. 6. Elongation at break of chitosan films against the number of UV passes with respect to soaking time

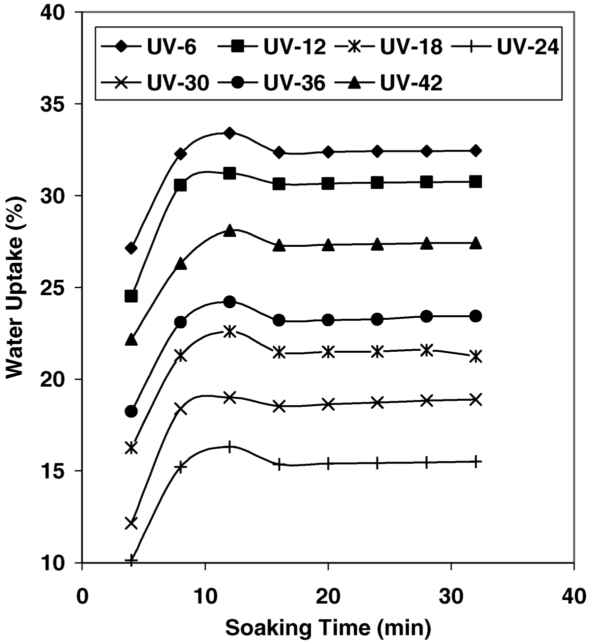


Fig. 7. Water uptake of optimized (S-2) chitosan films against immersing time with respect to number of UV passes.

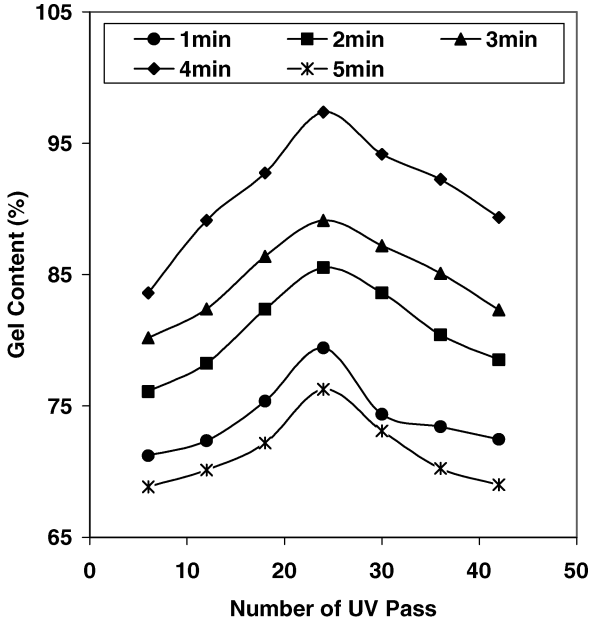


Fig. 8. Gel content (%) of cured chitosan films of different formulations against the number of UV passes with respect to soaking time.

It is clear that chitosan film treated with S-2 formulation showed higher TS but did not give higher Eb. The lowest Eb value was 6.12% at the 42nd UV pass for S-4 formulation containing 80% TSPMA. This was about 23.5% lower Eb compared to raw film. Silane increased high elasticity and impart some flexibility. Eb was very dependent on the nature of the formulation. The combination of TSPMA and MeOH at the ratio of 30% (S-2) yields the suitable conditions for better crosslinking phenomenon at the equilibrium condition that creates the chitosan film with highest TS and moderate Eb. It is to be noted that in all cases the Eb value decreased gradually as radiation intensities increased. This was because of radiation degradation of the films at the higher radiation intensities (20).

Chitosan films showed better performance in S-2 formulation (containing 30% TSPMA). Hence, to optimize the soaking time, S-2 formulation was used. The films were soaked for a different soaking time (1, 2, 3, 4 and 5 min) and then cured under UV radiation at different intensities (6, 12, 18, 24, 30, 36 and 42 passes). After 24 h of UV radiation PL, TS and Eb were investigated.

The PL values of S-2 treated chitosan films are plotted in Figure 4 against the number of UV passes as a function of soaking time. PL increased with the increase of soaking time and attained maximum at 4 min. After that, increasing soaking time decreaseed the PL values. PL values in all cases also increased with the increasing radiation intensities and showed best performance at the 24th UV pass and then decreased. The highest PL value was 45.1% at 24 UV passes for a 4 min soaking time. At the 24th UV pass, the PL values for 1, 2, 3 and 5 min soaking time were 19.1, 25, 38.1 and 24.1%, respectively. The lowest PL value was about 8% at the 42nd UV pass for a 1 min soaking time, which was about 82.2% lower compared to the highest PL value. Soaking time increased the cross-section area of the film and at the same time, the film surface becomes easy. As a result, the monomer can easily diffuse in the chitosan film and might react with the hydroxyl and amino group of chitosan in low swelling ratio (9).

In Figure 5, TS values are shown against the number of UV passes as a function of soaking time for S-2 formulation. The highest TS value of 28 MPa was found for a 4 min soaking time at 24th UV pass followed by 22.1 MPa for a 3 min soaking time at the same number of UV passes. TS value increased with the increase in soaking time, but started decreasing after 4 min soaking time. UV radiation has a similar effect on the TS values. At 6, 12, 18, 24, 30, 36 and 42 UV passes the TS of the chitosan films at 4 min soaking time were about 13.2, 18.2, 24.2, 28, 21.5, 16.8 and 10.2 MPa, respectively. Soaking led to increasing diffusion into the reaction sites and at the same time the amount of curing increased. On the contrary, at higher soaking time, the film became twisted, shrank and pale in appearance.

Figure 6 represents the Eb values of S-2 treated chitosan films against the number of UV passes as a function of soaking time. Eb values followed the similar trend like PL and TS. Eb value increased gradually with the increase in soaking time and showed the highest value at 4 min and then decreased. The highest Eb is 15% at the 24 UV passes for a 4 min soaking time. But soaking of chitosan films for 1, 2, 3 and 5 min showed about 66.6, 43.3, 6

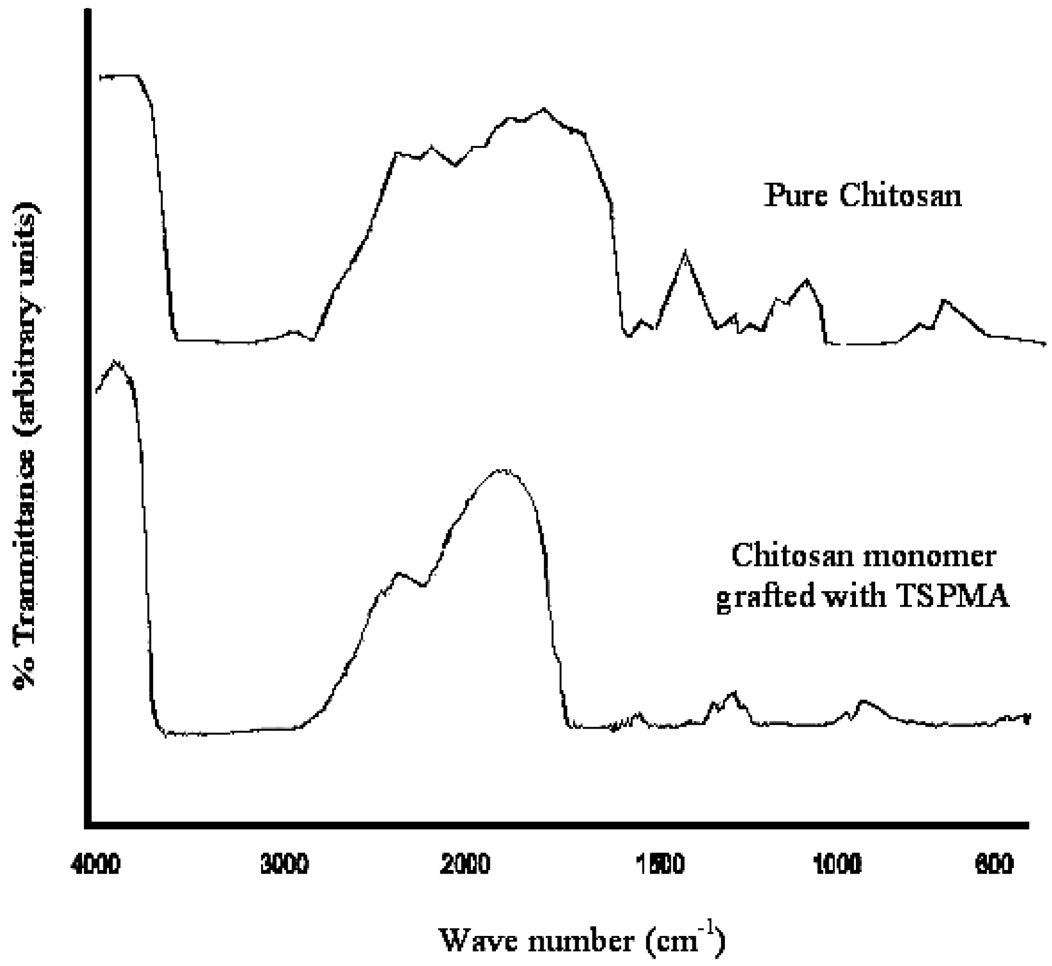
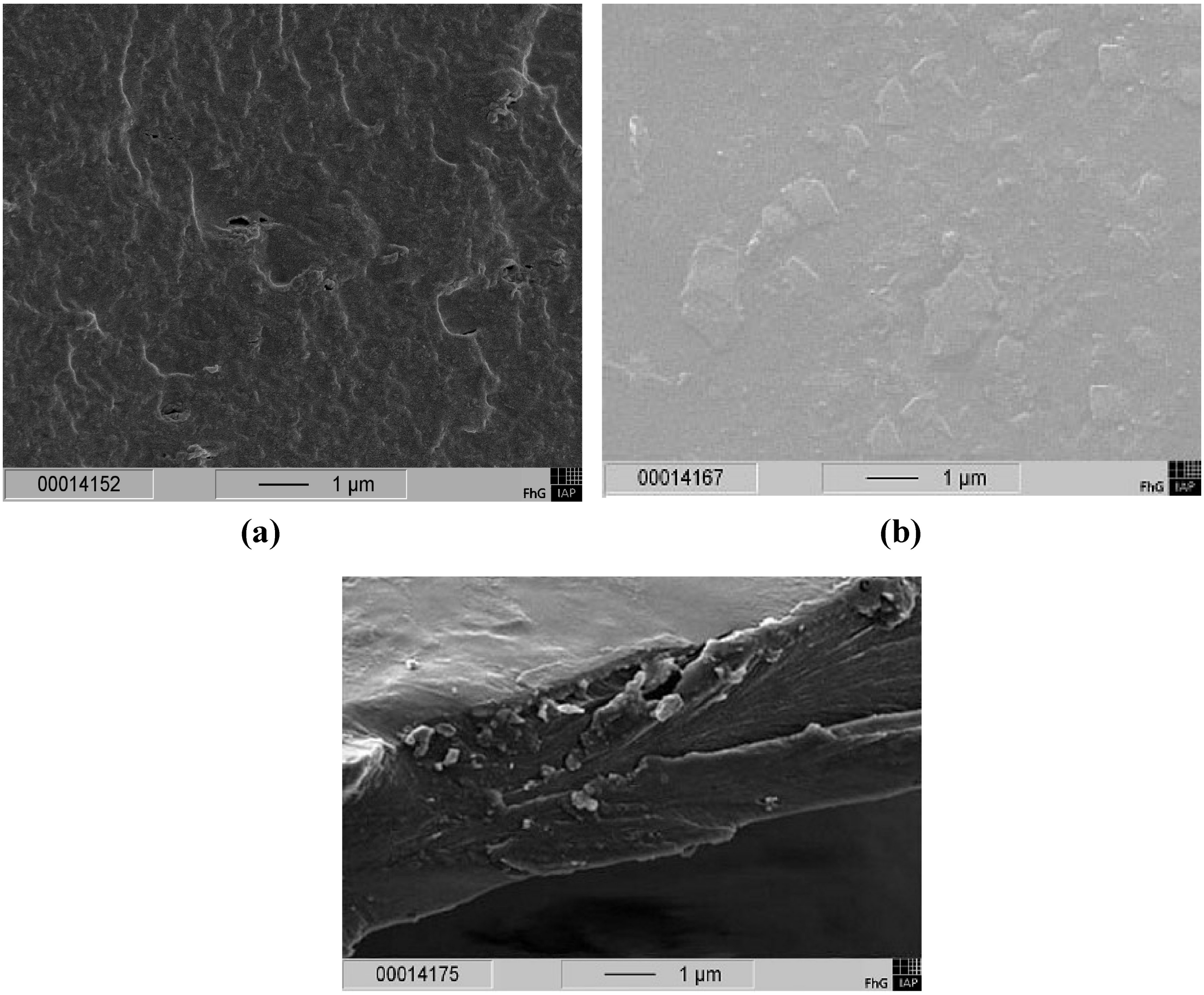


Fig. 9. FTIR Spectra of pure chitosan and TSPMA grafted chitosan film.

and 60% lower Eb, respectively compared to the highest Eb achieved in a 4 min soaking time. It indicates that, in a 4 minutes soaking time, the inherent character of the film appears to be superior as compared to other soaking times.

The percentage of water uptake of the S-2 treated chitosan film is plotted against a different immersion time as a function of UV radiation intensities in Figure 7. From the figure, it is observed, that during the first few minutes water uptake of the films was faster. After that, the water uptake capacity of the films slowed down and eventually almost reached a plateau. Chitosan film, which was cured under 6th UV pass, showed the highest water uptake, but at the 24th UV pass, the water uptake was at its minimum range. For 2 min of immersion time, the maximum value of water uptake was 33.4% (for the6th UV pass) while the minimum value was 16.3% (for the 24th UV pass). This was almost 51.1% reduction of water uptake value. This may be due to the crosslinking of the silane monomer (TSPMA) with chitosan, which lowered the void space in the polymer structure and impedes the water getting in. Thus, it was revealed that at the the 24th UV pass, water uptake of the S-2 treated chitosan films significantly reduced which supported higher TS and moderate Eb values of the cured film as explained above.

Gel content represents the crosslinking density of the cured films. The results of the gel content of the S-2 treated chitosan films are represented in Figure 8 against the number of UV passes as a function of soaking time. The gel content values increased with the increase of UV radiation intensities and after a certain UV dose (24 passes), the gel content decreased. The maximum gel content was obtained at the 24th UV pass for all soaking times but the highest gel content 95.3% was found for a 4 min soaking time at the 24th UV pass. Chitosan film showed the lowest gel content at the 42nd UV pass for 5 min soaking time and the value is 69%, which is about 27.5% lower compared to the highest value. At higher radiation intensities, the gel content of the films showed a lower value because of the radiation degradation of the films (9). Perhaps at higher radiation intensities more reaction sites become opened and make the film brittle.



(a) **(b)**

(c)

Fig. 10. Scanning electron micrographs of pure chitosan (a), TSPMA grafted chitosan (b) and cross-section of TSPMA grafted chitosan film.

Figure 9 showed the FTIR spectra of pure chitosan and TSPMA grafted photocured chitosan film. It is obvious from the spectra that molecular interactions did occur in both cured and uncured chitosan films. However, it is clearly seen from the spectra that by adding silane and UV irradiation, the chemical structure of chitosan had been changed significantly. Certain characteristic bands of chitosan had been eliminated or their intensity had been severely reduced. The first peak for chitosan at 898 cm^{-1} is assigned to the saccharide structure (21). The TSPMA grafted photocured chitosan film showed a shift in peak position and different peaks were obtained for the photocured chitosan film which was probably due to the TSPMA coating on the surface of the film. The TSPMA grafted chitosan film showed a peak at 2160 cm^{-1} due to the interaction of the OH group of TSPMA to the polysaccharide chain of chitosan.

The micrograph of pure chitosan film showed a rough and uneven surface (Fig. 10(a)). Neutralization of the acetate film with 1 *N* NaOH resulted in the shrinkage of the film to about 80% of its original dimensions. The dried chitosan film was flexible and had a thickness of 0.10 ± 0.01 mm. SEM photographs revealed a homogenous film surface with no gross defects. The chitosan film grafted with silane monomer showed a smooth surface as observed by SEM (Fig. 10(b)). The photocured film showed no pores or cracks on the surface. Cross-sections of photocured films showed homogenous surfaces, without separation of phases between the two polymers, and a compact structure in the film formation (Fig. 10(c)).

The homogenous matrix of photocured chitosan film is an indicator of the structural integrity of the observed films, and thus, adequate mechanical properties were obtained.

4 Conclusions

Chitosan was extracted from prawn shell waste to prepare the films. Then thin films were prepared by casting the 2% chitosan solution. Mechanical properties such as TS and Eb of the raw chitosan film were studied. It was found that, the raw chitosan film in water was not stable and became damaged. The films were treated with silane monomer (TSPMA) to improve the properties, followed by photo-curing technique. Chitosan films treated (4 min soaking time) with 30% TSPMA performed with better properties at the 24th UV pass and were 4 times higher TS value compared to raw chitosan film. It was also observed that optimized film showed lower water uptake. The SEM study showed homogenous surfaces, without separation of phases between the two polymers, and a compact structure in the film formation. The FTIR study revealed the intermolecular interaction among chitosan polysaccharide chain, TSPMA and water molecule in the film. Finally, it can be said that silane monomer improved the mechanical properties of the chitosan films.

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