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Effect of degree of deacetylation and molecular weight on physicochemical properties of chitosan films

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Chitosan is a linear natural polymer obtained by deacetylation of chitin using sodium hydroxide. Depending on the manufacturing process as well as its source, chitosan is commercially available in various types and grades with molecular weights (MW) ranging from 38 to 200 kDa and degree of deacetylation (DD) with a range between 60 to 100%. In this work, chitosan films of different degrees of deacetylation (DD) and molecular weights (MW) were prepared by the solution casting method at concentrations of 1%, 2%, and 3%. The influence of DD and MW were studied on the prepared films using various characterization techniques such as dressing pH, water absorption capacity, water vapour transmission rate (WVTR), porosity, and water contact angle (WCA). The water absorption capacity, water vapour transmission rate (WVTR), and porosity results showed that there were significant effects of DD, MW, and concentration on the above-mentioned films.

Keywords: Chitosan, degree of deacetylation, molecular weight, film.

Introduction

Chitosan is a natural polysaccharide consisting β (1→4) linkage D-glucosamine (N-acetyl-D-glucosamine). It is obtained by alkaline deacetylation of chitin. Chitin is a white, hard, inelastic, nitrogenous polysaccharide and is found in the exoskeleton as well as in the internal structure of invertebrates[1,2]. It can be converted into chitosan either by enzymatic or chemical reaction. It is the second most abundant natural polymer just after cellulose. It has also analogous structure of cellulose except acetamide groups (-$NHCOCH_3$) at C-2 positions[3–6]. Chemical deacetylation is more commonly used for commercial preparation due to low cost and feasibility of mass production. Chitosan is non-toxic, biocompatible, biodegradable, and hemocompatible. Due to these properties; it finds potential biomedical and industrial applications[7]. It also shows antibacterial properties against a broad spectrum of Gram-positive and Gram-negative bacteria. It is insoluble in aqueous solution where it is uncharged (pH > 6.5) or in solution containing high concentrations of multivalent anions[8]. Different types and grades of chitosan with different molecular weight and degree of deacetylation are available in the global market. These are prepared using various sources of chitin under different treatment conditions[9,10]. It has been reported that both the molecular weight and the degree of deacetylation of chitosan have significant effect on its functional properties namely solubility, viscosity, surface activity, and binding capacity[11]. In this study, chitosan films were prepared using different grades of chitosan and the effects of MW and DD on chitosan films were studied in terms of various physicochemical properties such as WVTR, porosity, dressing pH, water absorption capacity, and water contact angle.

Experimental

Materials:

Chitosan with degree of deacteylations >75% (CS1), >80% (CS2), and >85% (CS3) were purchased from Marine Hydrocolloids, Eranakulum, Kerala, India. The respective visocosities of each of the above 1% chitosan sample solutions are 1040 cps, 372 cps, and 618 cps. Glacial acetic acid was purchased from Sisco Research Laboratories Pvt. Ltd., New Mumbai, India. All chemicals were used without further purification.

Preparation of chitosan film:

Chitosan film was prepared by using solution casting method. Firstly, 1 g of chitosan powder was dissolved in 100

mL of 1% acetic acid solution and stirred continously to form clear solution. The clear solution was cast into the petri plate and dried in an oven to form film. The obtained film was stored in zip lock bag for further studies. Similar method was followed to prepare 2% and 3% chitosan films.

Fourier transform infrared spectroscopy (FTIR):

FTIR spectra of CS1, CS2, and CS3 samples were analyzed by using Perkin-Elmer spectrometer. The spectra of all samples were recorded in the range of 4000 cm^{-1} to 650 cm^{-1}.

Water vapour transmission rate (WVTR):

Water vapour transmission rate was determined gravimetrically at ambient temperature. The prepared film of circular shape was used to seal the openening of each beaker containing 15 mL of distilled water and the initial weight of each beaker was recorded. The weight loss of the beaker was monitored by weighing it after 24 h. Finally, the water vapour transmission rate (WVTR) was determined by using the following formula:

$$\text{WVTR (g.m}^{-2}\text{ day}^{-1}) = G/A\times T$$

where G represents weight loss, T is time (measured in hours during which the weight loss occurred), and A is the exposed area of the film.

Porosity:

The porosity of the films was determined using the liquid displacement method. In brief, weight of each dry film with a dimension of 20×20 mm was recorded (W_1) and then the film was immersed into a beaker containing hexane as a solvent until it was saturated (W_2). Thereafter, the film was removed carefully after 24 h and the solvent left in the beaker was weighed (W_3). The porosity of the film was determined using the following equation[9]:

$$\text{Porosity\%} = [W_2 - W_1 - W_3/W_2 - W_3]\times 100$$

Water absorption capacity[12]:

For the determination of water absorption capacity, a film with a dimension of 20×20 mm was weighed firstly and then the film was put into the beaker containing 20 mL of freshly prepared 0.9% saline solution at room temperature. Then swollen weight of the film was determined after removing excess surface water on the films with filter paper followed by placing them back into the same saline solution. Percentage swelling of the film was calculated according to the following equation:

$$\text{Water absorption (\%)} = [W_f - W_i/W_i]\times 100$$

where W_f is the weight of the swollen film and W_i is the initial weight of the film.

Water contact angle (WCA) measurements:

The water contact angle was determined by sessile drop method with the help of contact angle equipment (Pheomix 300) at ambient temperature.

Dressing pH:

Each film was separately immersed in normal saline solution till it reached equilibrium. After that each of the films was taken out from the same solution and it was used for recording the dressing pH of the film using digital pH meter (Model 152-R). All tests were performed in triplicate and average values were recorded.

Results and discussion

Fourier transform infrared spectroscopy (FTIR):

Fig. 1 shows the FTIR spectra of three chitosan samples with different degree of deacetylations (DDs) such as CS1, CS2, and CS3. It is clearly seen in this figure that there is no significant difference between the peaks obtained at particular frequencies for the said chitosan samples. Therefore, it is expected that all the chitosan samples with varying DDs mentioned here are derived from same chitin sample obtained from known source. Further, this phenomenon clearly indicates that deacetylation process does not change the inherent characteristics of chitosan itself. The characteris-

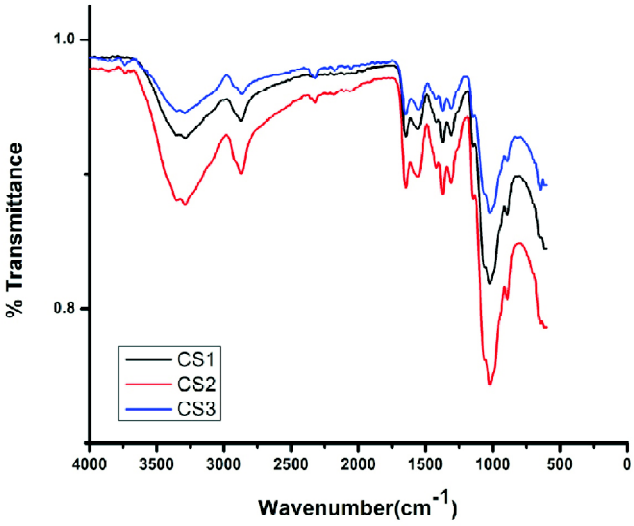

Fig. 1. FTIR spectra of CS1, CS2, and CS3 samples.

tics absorption peaks of all chitosan samples are illustrated in Table 1 for better clarity.

Table 1. Charcteristic peaks and frequencies of various grades of chitosan powder

Characteristics peaks	Wavenumber (cm^{-1})		
	CS1	CS2	CS3
OH and NH stretching	3286	3285	3287
C-H stretching	2872	2871	2867
C=O stretching (amide-I)	1647	1647	1647
N-H bending (amide-II)	1557	1556	1551
CH_3 bending vibration	1418	1419	1421
C-O-C stretching vibration	1147	1147	1147
C-OH bending vibration	1022	1021	1020

Water vapour transmission rate (WVTR):

Determination of water vapour transmission rate of any wound dressing material is needed to ascertain whether it will prevent excessive dehydration and also allow to build up of exudates. It is reported in literture that WVTRs in the range of 2000–2500 g/m^2/day would provide an adequate level of moisture that could not only prevent wound dehydration but also protect the wound from bacterial growth[13]. As shown in Fig. 1 that WVTR of the prepared films was in range between 500–2300 g/m^2/day. WVTR of the prepared film was compared with some synthetic commercially available wound dressings such as Intrasite (354±42 g/m^2/day), Tegaderm (491±44 g/m^2/day), and Bioclusive (382±26 g/m^2/day)[14,15]. Further, the results showed that the water vapour transmission rate of all types of chitosan decreased with increasing their individual concentrations from 1% to 3% as shown in Fig. 2. Further, it was found that 1% of CS2 showed the highest WVTR as compared to that of other films shown in Fig. 2. Moreover, 1% of CS2 showed significant WVTR as compared to that of CS1 and CS3.

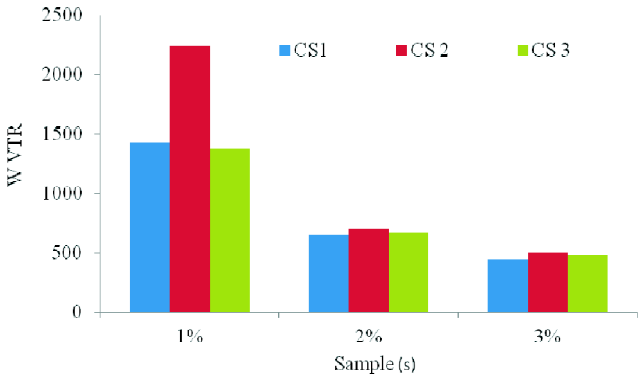

Fig. 2. WVTRs of the prepared films.

Porosity:

The porosity of the prepared films was studied by using liquid displacement method and hexane was used as a solvent. As shown in Fig. 3, it was found that the porosity of prepared films decreased with increasing the concentration from 1% to 3% and the similar trend was found in case of studying WVTRs of all the films made by various grades of chitosan. Further, it was found that there was no singificant effect of molecular weight and degree of deacetylation of various grades of chitosan regardless of their individual concentrations on porosity. Moreover, each grade of chitosan with concentration of 1% shows the highest porosity that is beneficial for wound dressing applications.

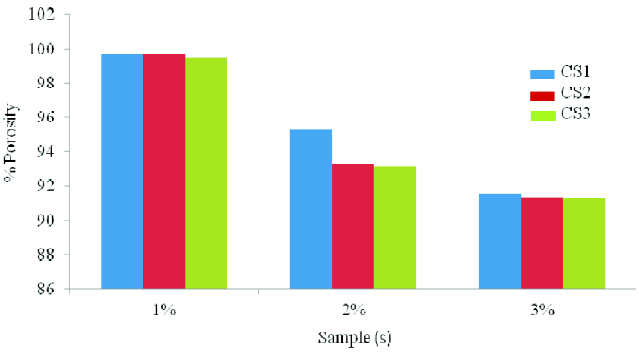

Fig. 3. Percentage porosity of the prepared films.

Water absorption capacity:

Water absorption capacity is an important factor of any wound dressing material that prevents dehydration of tissue, inhibits microorganism growth, etc. From the results shown in Fig. 4, it was found that the water absorption capacity of chitosan film decreased with incresing the concentration from 1% to 3% irrespective of DD and MW of chitosan. But the water absorption capacity of 1% CS2 film is little higher than that of other tested samples namely CS1 and CS3. Similar trend was also observed during WVTR study. These phenomena are notably good for any kind of wound dressing material.

Dressing pH:

The normal skin of a human body is acidic in nature and the pH of the human skin is ranging between 4 and 6.8. It is

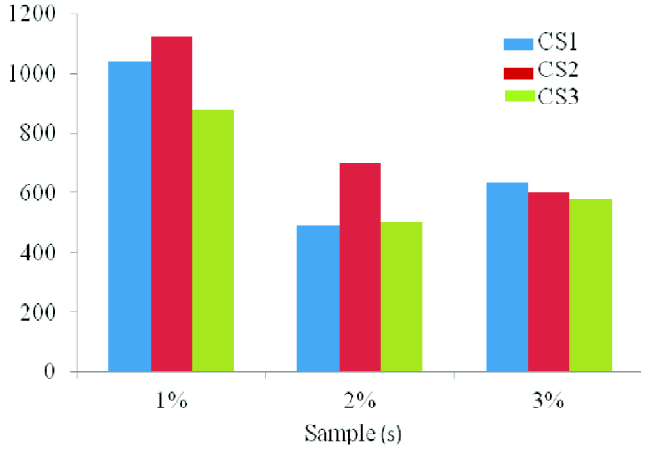

Fig. 4. Water absorption capacity of the prepared films.

reported in literature that slightly acidic environment at wound surface enhances the wound healing process as comapred to neutral and alkaline environment. As shown in Fig. 5, the pH values of all the prepared films were in the range between 6.10 and 6.27. Hence, the prepared films with slightly acidic pH could enhance the wound healing process.

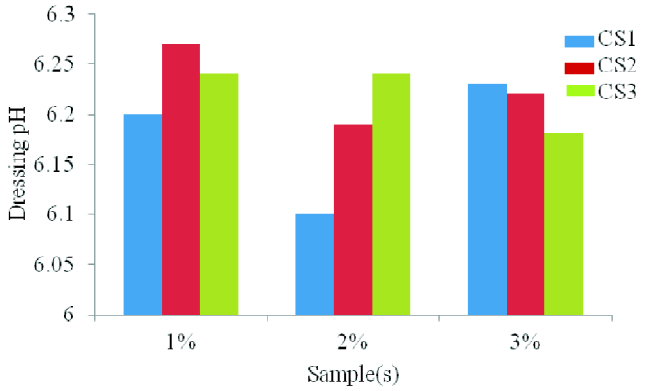

Fig. 5. Dressing pH of the prepared films.

Water contact angle:

Water contact angle was usually studied to check hydrophillic and hydrophobic nature of a substance. If a material has contact angle greater than 90°, it means that the material is hydrophobic in nature and if the same is less than 90°, it is meant to be hydrophillic in nature. The hydrophilic nature of any dressing materials enhances biocompatiblity as well as water abosorption capacity of the dressing materials. The results showed that the water contact angle of CS1, CS2, and CS3 of 1% chitosan films were

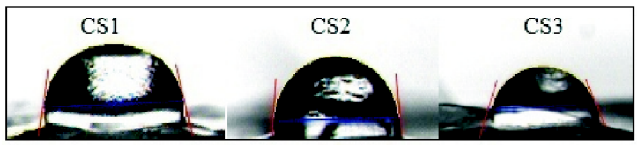

Fig. 6. Water contact angle of the prepared films.

78.86°, 76.76° and 67.64° respectively (Fig. 6). This result indicated that the prepared films are hydrophilic in nature.

Conclusions

The chitosan films prepared by conventional solution casting method. Effect of degree of deacetylation and molecular weight on physicochemical properties of various grades of chitosan films were studied. FTIR study showed that deacetylation process had no direct impact on inherent characteristics of chitosan. Further, chitosan films prepared with degree of deacetylation >75% showed high porosity as compared to other films. WVTR, porosity, water absorption capacity decreased with increasing the concentration of chitosan from 1% to 3%. Moreover, dressing pH result showed that the perpared films were slightly acidic in nature, which would improve wound healing process. In addition, water contact angle results indicated that all the chitosan films were hydrophilic in nature irrespective of their individual degree of deacetylation and molecular weight as well. Above all, in this study, 1% of CS2 showed improved physicochemical properties as compared to other chitosan samples.

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