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Solid-State and Mechanical Properties of Aqueous Chitosan-Amylose Starch Films Plasticized With Polyols

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ABSTRACT

The film-forming ability of chitosan and binary mixtures of chitosan and native amylose corn starch (Hylon VII) was evaluated with free films prepared by a casting/solvent evaporation method. Unplasticized and plasticized free chitosan films in aqueous acetic acid and respective films containing a mixture of chitosan and native amylose starch in acetic acid were prepared. Glycerol, sorbitol, and i-erythritol were used as plasticizers. Solid-state and mechanical properties of the films were studied by powder x-ray diffractometry (XPRD), differential scanning calorimetry (DSC), and a materials testing machine. The films composed of a mixture of chitosan and native amylose starch in acetic acid were clear and colorless. A plasticizer concentration of 20% wt/wt (of the polymer weight) was sufficient to obtain flexible films with all samples tested. X-ray diffraction patterns and DSC thermograms indicated an amorphous state of the films independent of the type of plasticizer used. In conclusion, incorporation of native amylose corn starch into chitosan films improves the consistency and the mechanical properties of the films.

KEYWORDS: chitosan, amylose corn starch, erythritol, free films, plasticizer

INTRODUCTION

Chitosan (Figure 1) is a cationic natural polysaccharide generally considered as a safe, biocompatible and biodegradable material.[1] During the past 20 years, chitosan has been evaluated for numerous pharmaceutical applications(eg, as a direct compression diluent, wet granulation excipient, wetting agent, gel and emulsion agent, and most recently as a film-coating agent. Higher molecular weight chitosans have been reported to have good film-forming properties as a result of intra- and intermolecular hydrogen bonding.[2] The chitosan film characteristics, however, varied from one report to another. Differences in the sources of chitin used to produce chitosan, chitosan material properties, solvents used, methods of film preparation, and types and amounts of copolymers and plasticizers used may affect the quality of the films.[3-6]

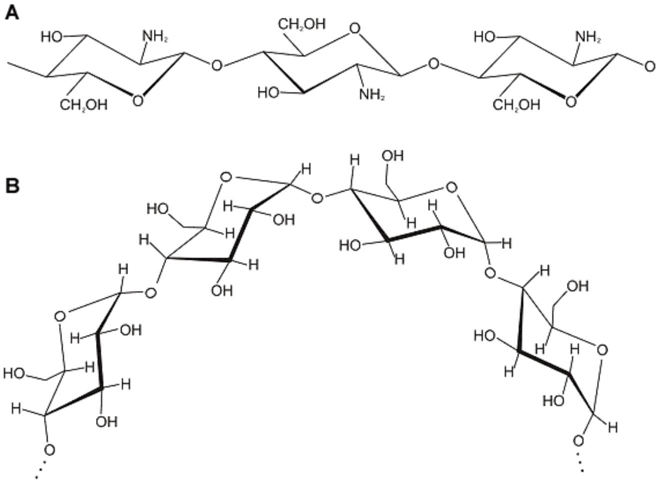

Figure 1. Chemical structure of chitosan (A) and native amylose corn starch (Hylon VII) (B).

Another natural polysaccharide, amylose starch (Figure 1), has also been investigated by several researchers using starch-based films cast from a solution or gel.[7-11] Wolff and collaborators[12] prepared self-supporting amylose films with and without glycerol plasticization. The influence of amylose content on the mechanical properties of cast films was studied by Lourdin et al.[8] They studied mixed amylose-amylopectin films and found slightly higher stress at break for plasticized amylose films but lower stress at break for plasticized amylopectin films with a glycerol/polymer ratio of 0.2. Moreover, according to Rindlav et al,[9] the functional

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Table 1. Effect of Plasticizer on the Thickness, Tensile Strength, and Percentage Elongation of Free Films (n = 5)

Property	Type of Plasticizer			
	Unplasticized	Glycerol	Erythritol	Sorbitol*
Thickness mm ± SD	0.019 ± 0.003	0.031 ± 0.004	0.028 ± 0.002	0.030 ± 0.004
Tensile Strength N/mm^2 ± SD	26.8 ± 2.0	27.2 ± 1.9	44.2 ± 2.0	-
Percentage Elongation at Break % ± SD	4.6 ± 1.9	5.4 ± 0.1	5.9 ± 1.6	-

*The films plasticized with sorbitol were very brittle and cracking.

properties of amylose films were, in general, slightly better than those of amylopectin films, regarding both film strength and barrier properties. More recently it was discovered that cross-linked starches possess unique features as an excipient for the manufacture of the controlled-release solid oral dosage form of drugs.[13,14]

Chitosan has also been assessed for its potentiality in the development of controlled-release systems and for its propensity for targeting drugs to specific sites.[15,16] Numerous control or sustained delivery systems with chitosan have been described in the literature.[17-21] The potentiality of chitosan in sustained-release systems has been assigned to its polymeric character, including its gel- and film-forming properties. Other polysaccharides (eg, pectin) have been evaluated for their susceptibility to combine with chitosan; there exists a potential of polyelectrolyte complex (PEC) formation between pectin and chitosan.[22,23]

There are no reports in the literature on the effects of the combination of chitosan and amylose starch polysaccharides on the film properties and drug release. In the present study, chitosan films prepared with amylose corn starch (Hylon VII) were evaluated with free films. The morphology, solid-state properties, and mechanical strength of the films and the effects of plasticizer (glycerol, sorbitol, or erythritol) were investigated.

MATERIALS AND METHODS

Materials

The film-coating materials studied were high molecular weight chitosan (Aldrich Chemical Company Inc., Milwaukee, WI, U.S.A) and amylose-rich corn starch, Hylon VII (National Starch & Chemical GmbH, Neustadt, Germany). Glycerol (European Pharmacopeia [PhEur]), sorbitol (PhEur), and i-erythritol (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), 20% wt/wt of the polymer weight, were used as plasticizers, and acetic acid (Riedel-de Haën, Seelze, Germany) and purified water as solvents.

Preparation of Free Films

Unplasticized and plasticized polymeric solutions (1% wt/wt) were prepared by dissolving chitosan in a diluted acetic acid (1%) solution at room temperature (21°C ± 2°C). The plasticizers (plasticizer content based on polymer weight = 20% wt/wt) employed were glycerol, sorbitol, and erythritol.

The aqueous polymer solutions contained 2% (wt/wt) of film former (mixture of chitosan and Hylon VII), glycerol or erythritol as a plasticizer (20% wt/wt of the polymer weight), acetic acid (1%), and purified water. The compositions of the chitosan-Hylon VII solutions studied were as follows: 100:0%, 80:20%, 60:40%, and 50:50% with glycerol; 100:0%, 80:20%, and 60:40% with erythritol.

Hylon VII solutions were prepared in a high-pressure reactor. In order to obtain the Hylon solutions, the suspensions were heated to 157°C, cooled down below 95°C, and filtrated. Details of the procedure are described elsewhere.[11] Hylon solutions were mixed with the chitosan solutions at ~50°C to 60°C.

For preparing free films, 8.0 g of the polymer solution was poured into polytetra-fluoroethylene (Teflon) molds (11 × 3.0 cm). A total of 10 to 12 molds per composition were originally made. The films were air dried for 4 hours at 60°C and allowed to stabilize in a desiccator for at least 24 hours at 21°C ± 2°C and 60% relative humidity (RH) before testing. The dry thickness of the films was measured at 5 locations (center and 4 corners) using a digital micrometer (Sony U30-F, Sony Magnescale Inc, Tokyo, Japan), and the mean thickness was calculated. The total number of replicates was 5. The results are summarized in Tables 1 and 2.

The cross sections of free films were studied by scanning electron microscopy (SEM). Samples for SEM were prepared by attaching the free films to double-sided carbon tape and coated 20 nm platinum with a sputter coater (Agar sputter coater B7340, Agar Scientific Ltd, Stansted, UK). The micrographs were taken with a Zeiss DSM 820 (Carl Zeiss, Oberkochen, Germany) SEM. An accelerated voltage of 10 kV and secondary electrons was used for all micrographs.

Table 2. Thickness of Free Chitosan

Type of Chitosan Films	Thickness (mm ± SD)
Chitosan-Hylon VII (100: 0%), glycerol	0.054 ± 0.003
Chitosan-Hylon VII (80: 20%), glycerol	0.051 ± 0.005
Chitosan-Hylon VII (60: 40%), glycerol	0.040 ± 0.001
Chitosan-Hylon VII (50: 50%), glycerol	0.039 ± 0.002
Chitosan-Hylon VII (100: 0%), erythritol	0.082 ± 0.003
Chitosan-Hylon VII (80: 20%), erythritol	0.043 ± 0.001
Chitosan-Hylon VII (60: 40%), erythritol	0.042 ± 0.002

Powder X-Ray Diffraction

Powder x-ray diffraction patterns on powders and free films were obtained by using an x-ray diffractometer (D8 Advance Bruker AXS GmbH, Karlsruhe, Germany) with CuKα radiation (1.54 Å). The samples were scanned from 5° to 40° (2θ) with an increment of 0.02° and measurement time of 10 s/increment. Determination of crystallinity was based on the assumption that the experimental intensity curve is a linear combination of a crystalline component and an amorphous component. The crystallinity of the samples was estimated by fitting the intensity of the crystalline component and the amorphous material to the experimental curve, and it was obtained as the ratio between the integrals of the intensities of the crystalline component and the studied sample.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) thermograms of chitosan powder and free films were measured using a differential scanning calorimeter (model 910 DSC, TA Instruments, New Castle, DE). Samples of 2 to 5 mg were accurately weighed into solid aluminum pans without seals. The measurements were obtained at a heating rate of 10°C/min and scanning from 60°C to 400°C.

Mechanical Strength Measurements

A Lloyd LRX materials testing machine (Lloyd Instruments Ltd, Fareham, UK) was used to determine the mechanical properties of free films. The films were cut into 11 × 1.5 cm strips for testing. The measurements were performed using a 2000 N load cell and a cross-head speed of 5 mm/min. Five parallel determinations were made for each sample. The tensile stress was plotted against the percentage of elongation to give a stress-strain curve, and the ultimate tensile strength as well as the percentage of elongation at break was reported.

RESULTS AND DISCUSSION

Scanning electron micrographs of cross-sections of free films are presented in Figure 2. These figures indicate that the structure of films was homogeneous and continuous and thus the films were suitable for further evaluation.

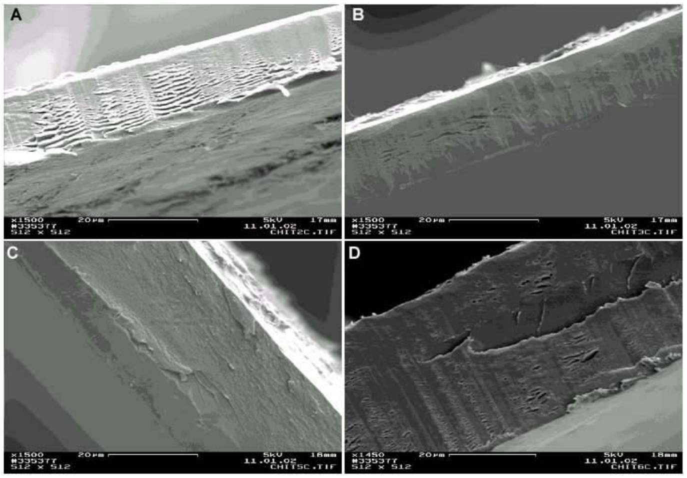

Figure 2. Scanning electron micrographs on cross-sections of free chitosan films containing glycerol (A), erythritol (B), chitosan and Hylon VII (60:40) and glycerol (C), as well as chitosan and Hylon VII (80:20) and erythritol (D).

All chitosan films were clear and colorless to pale yellow. The films, especially those prepared with sorbitol, were smooth and very brittle. The plasticizer concentration used was the same for all films tested (20% wt/wt based on the polymer weight) and sufficient to obtain flexible films with all samples. Films produced from the unplasticized solutions were thinner and were easy to remove from the mold. The incorporation of amylose corn starch increased the thickness of the films.

Solid-State Properties and Thermal Behavior

As seen in Figure 3, the powder x-ray diffraction pattern of chitosan powder showed diffraction peaks at ~10° (2θ) and 20° (2θ). The high molecular weight chitosan was in crystalline state. When processing chitosan powder into films, an amorphous state of the films independent of the type of plasticizer used was observed. The intensity of the hydrated crystal peak at ~20° (2θ) was higher than that at ~10° (2θ).

Amylose is known to recrystallize into the type-B crystalline form from a dilute solution. Gidley[24] proposed that the origin of amylose gelation lies in the formation and subsequent aggregation of interchain type-B double helices. Figure 4 shows the effect of incorporation of Hylon VII to chitosan films. The free films maintain an amorphous state. None showed any specific diffraction peaks at 2θ to type B (5.6°, 15°, 17°, 22°, and 24°),[25] thus Hylon VII remained in an amorphous state. It may be concluded that all films of binary mixtures of chitosan and Hylon VII were in an amorphous state. Nunthanid et al[6] found that the chitosan (lower and higher molecular weight) films prepared by casting from aqueous acetic solution were in amorphous to partially crystalline form.

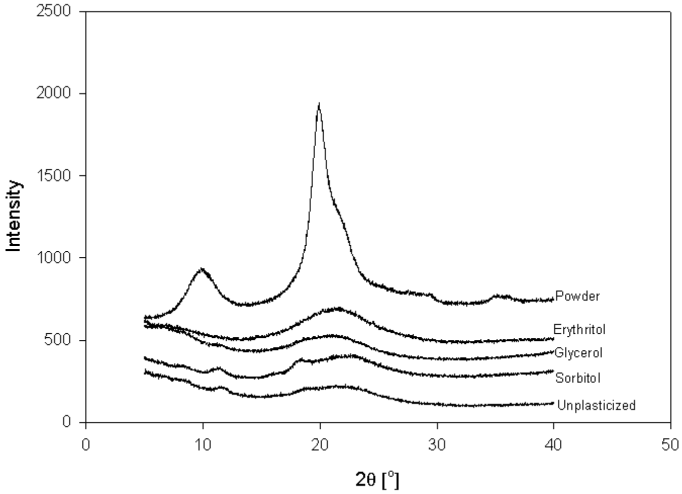

Figure 3. X-ray diffraction patterns of chitosan powder and chitosan films. From bottom to top: unplasticized films, films plasticized with sorbitol, glycerol, and erythritol, and high molecular weight chitosan powder.

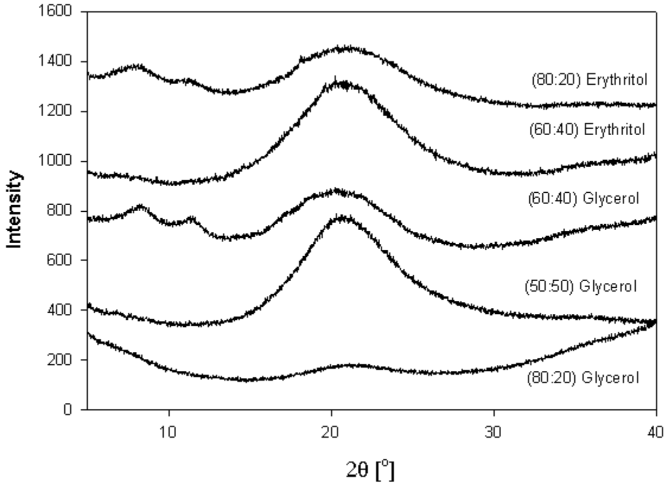

Figure 4. X-ray diffraction patterns of chitosan-Hylon films (80:20) and glycerol, (50:50) and glycerol, (60:40) and glycerol, (60:40) and erythritol, and (80:20) and erythritol.

DSC thermograms of chitosan powder and films exhibited exothermic peaks at 280°C to 300°C, indicating polymer decomposition. Processing of chitosan powder into films resulted in degradation at a lower temperature. The endothermic peaks that occur over a large temperature range (~35°C-160°C), attributable to water loss, represent the energy required to vaporize water present in the film samples. Lim and Wan[3] reported the exothermal decomposition peaks of chitosan flakes and films. Nunthanid et al[6] reported that all chitosan films were degraded at <280°C to 300°C, which agrees well with the results of our study. Chitosan molecules have a strong affinity for water molecules. Chitosan films have a higher affinity for water compared with the powder, probably because the chitosan molecules in the films are protonated, rendering the films more hydrophilic than the powder.[3]

The absence of other endotherms in the DSC thermograms, besides the one at ~35°C to 160°C, implied that the chitosan films were amorphous. This was also confirmed by the x-ray diffraction results.

Mechanical Properties

The tensile strength and the elongation at break of free chitosan films are summarized in Table 1. The most suitable plasticizer was erythritol with the greatest tensile strength. Erythritol decreases the rigidity of the network, producing a less ordered film structure and increasing the ability of movement of polymer chains. Films of suitable toughness and flexibility may thus be obtained. The addition of erythritol enhanced the plasticization and resulted in a highly amorphous polymer film structure. Chitosan films plasticized with sorbitol were very brittle and cracking. In general, the crystallinity of a film structure promotes intermolecular forces, thus increasing the rigidity and brittleness of the film, and the crystallinity of sorbitol-plasticized films was the highest. The mechanical properties of chitosan/polyvinyl alcohol (PVA)/H_2O and chitosan/gelatine with or without polyols, sorbitol, and sucrose were studied by Arvanitoyannis et al.[26,27] The tensile strength decreased proportionally to the plasticizer content, whereas the percentage elongation increased considerably, particularly in the case of sorbitol.

Studies on the effect of molecular weight on the chitosan film characteristics have reported that the mechanical strength of the film increased with increasing molecular weight of chitosan.[6] This finding might be attributable to an entanglement network forming during film formation of higher molecular weight chitosan. Glycerol is a commonly used plasticizer in chitosan acetate films. It improves the mechanical properties of free films.[4] Remuñán-López and Bodmeier[4] reported that films made of chitosan acetate were significantly less flexible than those made of chitosan glutamate at any investigated glycerol content (0%-30%), thus they were better plasticized by glycerol.

As shown in Figures 5 and 6, the increase of Hylon VII concentration increased the values of tensile strength for both glycerol- and erythritol-plasticized films, but at concentrations higher than ~20% the results of tensile strength decreased. The Hylon VII concentration did not affect the elongation at break, particularly in the films plasticized with erythritol. Free films containing 50% wt/wt of Hylon VII were soft, weak, and difficult to remove from the molds; consequently, this was the maximum concentration of Hylon VII evaluated to obtain flexible films. The variations in the percentage of elongation of films with erythritol were lower compared with the results obtained with glycerol.

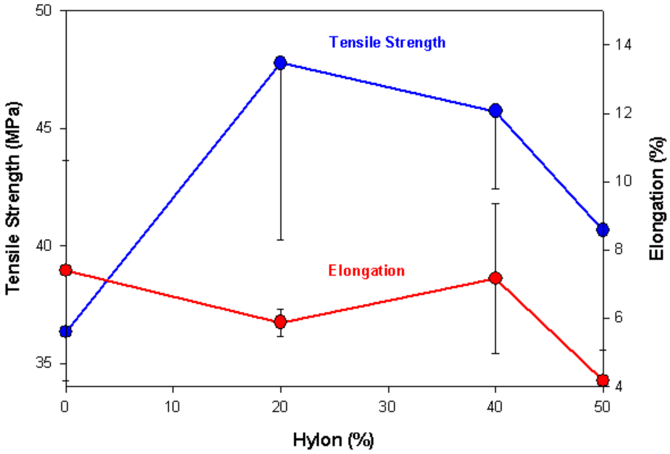

Figure 5. Tensile strength and elongation profiles of free chitosan films containing Hylon VII 0%-50% and glycerol as a plasticizer (n = 5).

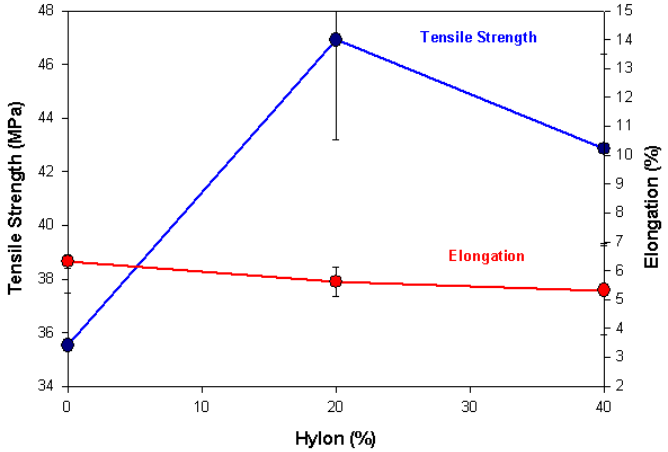

Figure 6. Tensile strength and elongation profiles of free chitosan films containing Hylon VII 0%-40% and erythritol as a plasticizer (n = 5).

Although, DSC and powder x-ray diffraction techniques confirmed that all films of binary mixtures of chitosan and Hylon VII were in an amorphous state, according to x-ray diffraction patterns of chitosan, Hylon VII (50:50) films plasticized with glycerol and (60:40) plasticized with erythritol showed a higher degree in molecular arrangement around 20° (2θ) (Figure 4). Therefore, it is evident that the molecules of film formers start to rearrange and probably crystallize, consequently affecting the mechanical properties of the films. It is expected that erythritol is a promising plasticizer to be used with the film coatings of the present binary mixtures. However, more information is needed, for example, on the physical stability of the present films plasticized with polyols.

The present films can be used, for example, in special, multilayered, complex, controlled-release systems for oral site-specific drug delivery. Another application could be the film coatings to obtain enhanced oxygen and gas barrier properties as amylose starch has been shown to form films with a high resistance to oxygen.[28]

CONCLUSION

Flexible and mechanically strong films can be prepared with aqueous binary mixtures of chitosan and amylose corn starch (Hylon VII) plasticized with polyols. The film properties such as morphology, mechanical strength, and crystallinity are dependent on the film former to film former ratio and on the plasticizer (polyol) used.

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