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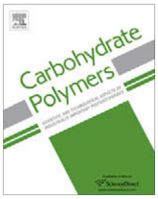

Short communication

Hydrated salts as both solvent and plasticizer for chitosan

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ABSTRACT

Some hydrated salts were determined to act as both solvent and plasticizer for chitosan. Chitosan was dissolved in aqueous salt solutions of high-valent cations (aluminium(III), iron(III) and chromium(III)) and dissolved almost completely in aqueous salts containing 3.10 mmol salts/g chitosan. Hydrated salts plasticized chitosan and aqueous aluminium(III) chloride/chitosan solution yielded plasticized films with the highest maximal tensile stress and elongation at break point, 71.9 MPa and 275%, respectively. The humidity dependence of dynamic viscoelastic properties and water content suggests that water plays an important role in the plasticization of chitosan and the water content required for such is approximately 20 wt.%. The addition of hydrated salts accelerates plasticization of chitosan, because sufficient water is available due to the presence of the salts.

1. Introduction

Chitosan [β-(1,4)-2-amino-2-deoxy-D-glucopyranose] is the deacetylated product of chitin, which is the second most abundant biopolymer in nature next to cellulose (Shahidi, Arachchi, & Jeon, 1999) and is found in the exoskeleton of crustaceans, fungal cell walls and other biological materials. Compared with other polysaccharides, chitosan exhibits various pharmacological activities, such as bacteriostasis (Chen, Yeh, & Chiang, 1996; Coma et al., 2002; Helander, Nurmiaho-Lassila, Ahvenainen, Rhoades, & Roller, 2001; Knowles & Roller, 2001; Moller, Grelier, Pardon, & Coma, 2004; Tsai & Su, 1999), fungistasis (Roller & Covill, 1999). However, utilization of chitosan is very difficult to achieve, due to its insolubility in pure water and in common organic solvents. On the other hand, some solvents for chitosan have been ascertained, and they are summarized in Table 1. Chitosan dissolves in trifluoroacetic acid (Hasegawa, Isogai, Onebe, & Usuda, 1992), various aqueous solutions containing mineral or organic acids (Muzzarelli, 1977), and carbon dioxide (Sakai, Hayano, Yoshioka, & Yoshioka, 2001), because it is a basic polymer. The dissolution of chitosan in dimethylsulfoxide requires a lyophilizing process and salt formation with sulfonic or salicylic acid (Sashiwa, Shigemasa, & Roy, 2000). Hexafluoro-2-propanol (HFP) dissolves chitosan directly by the interaction of the fluoride moiety in HFP with the intra- and intermolecular hydrogen bonds in chitosan (Sashiwa, Kawasaki, Nakayama, Muraki, & Aiba, 2002). Chitosan dissolved in these solvents forms viscous solutions that can be used for the preparation of films or fibers by evaporation of the solvents. Unfortunately, chitosan films or fibers are hard and brittle (Cheung, Wan, & Yu, 2002; Suyatma, Copinet, Tighzert, & Coma, 2004), and therefore require plasticizers to increase material flexibility. Glycerol (Coffin & Fishman, 1993), sorbitol (Arvanitoyannis, Kolokuris, Nakayama, Yamamoto, & Aiba, 1997) and poly(ethylene glycol) (Zhang, Li, Gong, Zhao, & Zhang, 2002) are commonly used as plasticizers for chitosan.

It was determined that hydrated salts can act as both solvents and plasticizers for chitosan; therefore, a new dissolution/plasticization system for chitosan is presented. Using water and salt, particularly aluminium(III) or iron(III), chitosan can dissolve almost completely. Of these salts, hydrated salts can be used to plasticize chitosan. This knowledge will be able to contribute to the improvement in manufacturing environments and reducing costs. Thus the use of hydrated salts rather than mineral and organic acids as solvents for chitosan can reduce odors and corrosion from the evaporation of acids. If chitosan can be plasticized by the addition of such salts, then further addition of plasticizers becomes unnecessary. The main objective of this study was to evaluate the solubility of chitosan in aqueous salt solution and investigate the effect of plasticization on the mechanical properties of the chitosan films prepared by a casting/solvent evaporation process.

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Table 1
Reported solvents for chitosan.

Mineral acids and organic acids	Muzzarelli (1977)
Trifluoroacetic acid	Hasegawa et al. (1992)
Dimethylsulfoxide	Sashiwa et al. (2000)
Carbon dioxide	Sakai et al. (2001)
Hexafluoro-2-propanol	Sashiwa et al. (2002)

2. Experimental

Chitosan from crustaceans, with a molecular weight of 200,000 and a degree of deacetylation above 80%, was obtained from Tokyo Chemical Industry (Tokyo, Japan) and used after drying *in vacuo*. Special reagent grade salts were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. Distilled water was used to prepare all solutions. Chitosan (1 g) was added to a rapidly stirred water (100 mL, 50 °C) containing salts (salts: $FeCl_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $AlCl_3{\cdot}6H_2O$, and $Al(CH_3CHOHCOO)_3$, concentrations: 3.10, 4.65, and 6.20 mmol salts/g chitosan). After 24 h, the viscous solution was filtered through a stainless mesh (100 mesh) to remove undissolved fractions. The solubility of chitosan in the aqueous salt solution was defined as solubility of chitosan (wt.%) = $(1 - W_{UD}) \times 100$, where W_{UD} is the dried weight of the undissolved fraction. The filtrate was evacuated to remove trapped air bubbles, and poured onto a poly(methyl methacrylate) plate. The films were air-dried for 48 h under ambient conditions. Pure chitosan films were prepared as follows. Chitosan (1 g) was dissolved in a 2 wt.% aqueous acetic acid solution (100 mL). The mixture was poured onto a poly(methyl methacrylate) plate and dried at room temperature. The film obtained was soaked in a 0.5 N NH_3 solution, washed with deionized water and then dried. Films of ca. 50 μm thickness were obtained and conditioned with 50% relative humidity (RH) at 23 °C for 24 h. Tensile tests were performed using a tensile testing machine (Imoto-Machinery, Kyoto, Japan) with a crosshead speed of 5 mm/min. Sample films for the tensile tests were cut (14 × 2 mm) using a dumbbell-shaped knife. At least three samples of each type of film were tested. The humidity dependence of the dynamic viscoelastic properties was measured using a dynamic viscoelastometer (DVA-225, IT Keisoku Seigyo, Osaka, Japan). The relative humidity was controlled as a linear function of time with increasing humidity at a rate of 1%RH/min at 60 °C. The frequency of the tensile strain applied to the sample was 10 Hz. To determine the water content of films stored for 24 h under a given condition in temperature and humidity chamber (SH-240, ESPEC corp., Osaka, Japan), film samples of approximately 500 mg were dried in a vacuum oven at 100 °C for 12 h. The weight loss of the sample was determined, from which the water content (WC) was calculated using the equation WC (wt.%) = $(M_i - M_d)/M_d \times 100$, where M_i and M_d are the masses of initial and dried samples, respectively.

3. Results and discussion

The results of solubility tests for chitosan in various aqueous salt solutions are summarized in Table 2. Dissolution of chitosan was ascertained by the increase in viscosity of the salt solution. The results suggest a tendency for chitosan to dissolve in aqueous salts consisting of high-valent cations (aluminium(III), iron(III) and chromium(III)), except for aluminium(III) sulfate. The viscosity of the chromium(III) nitrate solution was increased by addition of chitosan; however, there were many undissolved fractions in the solution, which suggests that the solubility of chitosan in chromium(III) nitrate solution is very low, and therefore chromium(III) nitrate was excluded as a target solution in this investigation. It is considered that the mechanism for the dissolution of chitosan is attributed to the acidic character of these salts in solution. The pH values of the solution are given in Table 3. Acidic salt is hydrolyzed to corresponding acid and metal hydroxide in water. Therefore chitosan dissolves in these aqueous salt solutions by formed acid. Insolubility of chitosan in aluminium(III) sulfate solution caused by the fact that chitosan is not dissolved in sulfuric acid. The solubility of chitosan in the aqueous salt solutions is given in Table 3. Chitosan was almost completely dissolved in aqueous salt solutions containing 3.10 mmol salts/g chitosan. The highest chitosan solubility was obtained for an aqueous solution of iron(III) chloride. It may be presumed that pH of aqueous salts is one of the factor on the dissolution capability of chitosan. It has become apparent that using about 1 wt.% aqueous salt solutions, particularly aluminium(III) or iron(III), chitosan can be dissolved very easily forms viscous solution.

Table 2
Solubility of chitosan in various aqueous salt solutions.

Salt	Solubility[a]	Salt	Solubility[a]
$AlCl_3{\cdot}6H_2O$	++	$Cr(NO_3)_3{\cdot}9H_2O$	+
$Al(NO_3)_3{\cdot}9H_2O$	++	$CuSO_4{\cdot}5H_2O$	–
$Al(CH_3CHOHCOO)_3$	++	$Ni(NO_3)_2{\cdot}6H_2O$	–
$Al_2(SO_4)_3{\cdot}16H_2O$	–	$Co(NO_3)_2{\cdot}6H_2O$	–
$FeCl_3{\cdot}6H_2O$	++	$MgCl_2{\cdot}6H_2O$	–
$FeCl_2{\cdot}4H_2O$	–	$CaCl_2$	–

[a] Solubility: [++] viscosity of the solution increase and almost dissolve; [+] viscosity of the solution increase and partially dissolve; [–] no change.

The maximal tensile stress (TS) and elongation at the break point (E_b), and the water content (WC) of chitosan films are summarized in Table 4. All of the final target aqueous salt solutions, except for aluminium(III) lactate, were effective in plasticizing the chitosan films. Increasing salt (except for aluminium(III) lactate) concentration tended to increase E_b, WC and decrease TS. On the contrary, for chitosan films containing aluminium(III) lactate, the WC decreased with increasing concentration and the film became more brittle than the pure chitosan films. It is considered that the plasticization of chitosan films is related to the hydration water of the salts, because all of the target salts except for aluminium(III) lactate form hydrates. In addition, mechanical properties of these films with different salts can be compared at almost the same water content, specifically, the TS and E_b of $FeCl_3$ are lower and higher, respectively, than those of $Al(NO_3)_3$ and $AlCl_3$ at water content of 28 ± 2%, indicating that plasticization is greatly affected by $FeCl_3$ besides water. The mechanism for plasticization by salts is discussed later. Among the salts tested, aluminium(III) chloride resulted in films with the highest TS (71.9 MPa, 3.10 mmol salt/g chitosan) and E_b (275%, 4.65 mmol salt/g chitosan).

Stress–elongation curves for pure chitosan film and chitosan films containing various concentrations of aluminium(III) chloride are plotted in Fig. 1. The stress–elongation curve for pure chitosan film showed a typical pattern for a brittle material. However, the chitosan films containing aluminium(III) chloride exhibited stress–elongation behavior similar to that for ductile polymers. The chitosan film containing 3.10 mmol aluminium(III) chloride/g chitosan exhibited a yield point, whereas the yield point disap-

Table 3
Solubility of chitosan in target salt solutions and pH values of salt solutions.

Amounts of salt (mmol/g chitosan)	Solubility (%) [pH value of salt solution [a]]			
	$FeCl_3{\cdot}6H_2O$	$Al(NO_3)_3{\cdot}9H_2O$	$AlCl_3{\cdot}6H_2O$	$Al(CH_3CHOHCOO)_3$
1.55	99.4, [2.2]	87.8, [3.3]	89.9, [3.3]	62.3, [3.6]
3.10	99.9, [1.9]	99.8, [3.1]	99.9, [3.1]	96.6, [3.5]

[a] The pH value of salt solution (without chitosan) measured at 25 °C.

Table 4
Effect of salt on maximal tensile strength (TS), elongation at the break point (E_b) and water content (WC) of chitosan films (23 °C, 50% RH).

Amounts of salt (mmol/g chitosan)	$FeCl_3 \cdot 6H_2O$			$Al(NO_3)_3 \cdot 9H_2O$			$AlCl_3 \cdot 6H_2O$			$Al(CH_3CHOHCOO)_3$		
	TS (MPa)	E_b (%)	WC (wt.%)	TS (MPa)	E_b (%)	WC (wt.%)	TS (MPa)	E_b (%)	WC (wt.%)	TS(MPa)	E_b (%)	WC (wt.%)
0.00 (pure chitosan)[a]	63.3	3.7	9.7	←			←			←		
3.10	46.3	2.3	20.9	70.0	4.1	26.1	71.9	36.0	29.2	Brittle[b]		32.9
4.65	36.3	34.8	22.9	21.7	95.3	70.5	14.1	275	36.2	Brittle[b]		27.8
6.20	26.3	71.2	28.0	14.6	117	102	10.7	199	44.0	Brittle[b]		24.4

[a] Salt free chitosan films (pure chitosan) were prepared from aqueous acetic acid solution.
[b] Tensile tests could not be performed due to brittleness of the films.

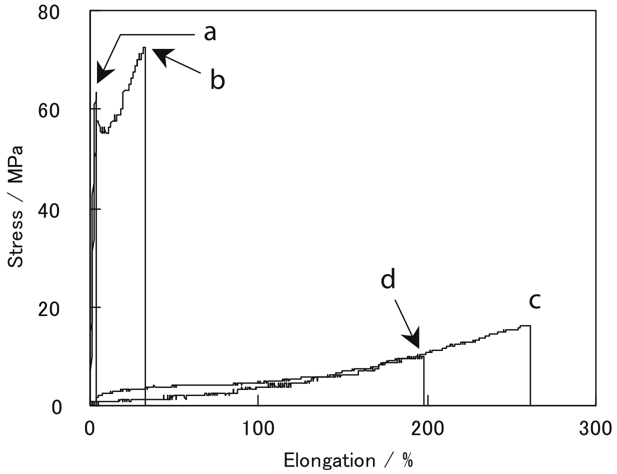

Fig. 1. Stress–elongation curves for (a) pure chitosan film and chitosan films containing aluminium(III) chloride at (b) 3.10, (c) 4.65, and (d) 6.20 mmol/g chitosan.

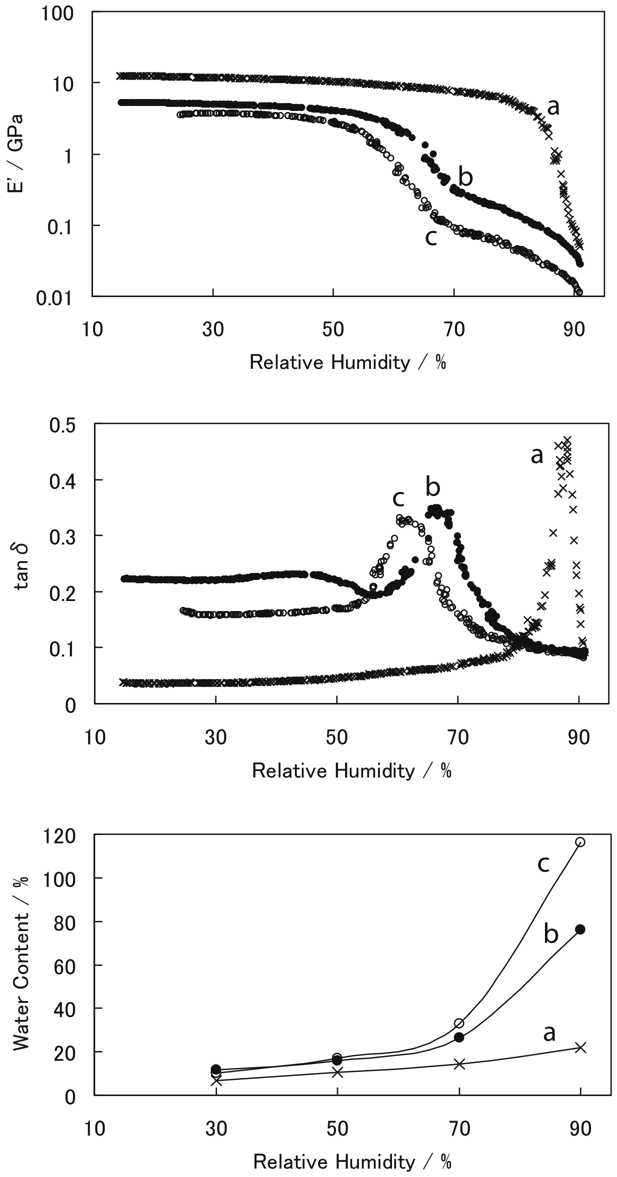

Fig. 2. Humidity dependence of E', tan δ and water content measured for pure chitosan films (a) and chitosan films containing iron(III) chloride at (b) 3.10, and (c) 4.65 mmol/g chitosan at 60 °C.

peared in the stress–elongation curves of chitosan film containing 4.65 or 6.25 mmol aluminium(III) chloride/g chitosan. This suggests that these salts can improve the elastic properties of chitosan, similar to the addition of poly(ethylene glycol) (Alexeev, Kelberg, Evmenenko, & Bronnikov, 2000; Suyatma, Tighzert, Copinet, & Coma, 2005).

The humidity dependence of dynamic viscoelastic properties (Zhou, Tashiro, & Li, 2001a, 2001b; Zhou et al., 2001c) was measured for the pure chitosan film and chitosan films containing iron(III) chloride. To estimate the variation of WC during the measurement, the WC in the chitosan films was determined, and the results are shown in Fig. 2. As the humidity was increased, E' decreased abruptly, the damping characteristics (tan δ) showed peaks at the corresponding humidity, and the WC increased exponentially. It is presumed that chitosan films are plasticized at the humidity of maximal tan δ (Yano, 1993) and the tan δ peaks probably correspond to a molecular relaxation. The result for the pure chitosan film suggests that chitosan films are plasticized by absorbed water. Therefore, it can be presumed that a chitosan film containing water at ca. >20 wt.% is plasticized. This threshold is almost compatible with hydrophilic polymer (NaCMC) (Yano, 1993). Lourdin et al. reported antiplasticization effect, such as a decrease in tensile elongation, of starch films, which is caused by water/glycerol plasticizer mix at low contents of it (0–15%) (Lourdin, Bizot, & Colonna, 1997); however, the effect was not observed for chitosan/hydrated salts systems probably because of relatively high water contents (ca. >20 wt.%). The humidity at the maximal tan δ shifted toward the lower humidity side with increasing salt content in the chitosan film.

Chitosan films are plasticized at lower humidity by the addition of salts, because the chitosan films contain sufficient water (ca. >20 wt.%) at low humidity due to the presence of hygroscopic salts. From these results, it can be presumed that water plays an important role in the plasticization of chitosan, and chitosan films containing salts are plasticized by excessive absorption of water (bulk or free water). However, as shown in Table 4, despite sufficient water for plasticization included in the chitosan film containing aluminium(III) lactate, the film became more brittle. This phenomenon is anticipated to result from chitosan–metal interac-

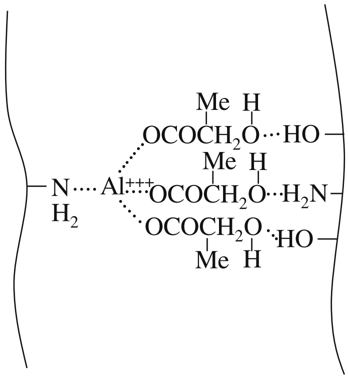

Fig. 3. Schematic crosslinking of chitosan molecule by aluminium(III) lactate.

tion (pendant–model complex of chitosan and metal salt) (Mochizuki, Sato, Ogawara, & Yamashita, 1989; Ogawa, Oka, & Yui, 1993). As shown in Fig. 3, we proposed the structure of closslinking. Thus aluminium ion forms a complex with the amino group of chitosan molecule, and the crosslinking of chitosan results from the hydrogen-bonding interaction between the hydroxyl group in the lactate ion and the hydroxyl or amino group of chitosan molecule. Consequently, the chitosan film became more brittle. On the other hand, when the counteranion is Cl^- or NO_3^-, the crosslinking by the salt is impossible. Therefore, the salts ($FeCl_3$, $Al(NO_3)_3$ and $AlCl_3$) themselves may contribute to the plasticization of chitosan by the ionic repulsion and/or the steric hinderance of the chitosan–metal complex. For example, plasticization of starch by sodium chloride has been reported (Farahnaky, Farhat, Mitchell, & Hill, 2009). Further, since these salts form hydrates, the addition of these salts accelerates the plasticization of chitosan, due to the hydration water of the salts. Interaction between chitosan and a hydrated salt may be reduced by the hydration (coordination) water of the salts, and thereby, adsorbed water contributes to the efficient plasticization of chitosan.

Chitosan films containing the hydrated salts exhibited excellent mechanical properties, and several of these chitosan films possessed mechanical properties comparable to synthetic polymers (polyethylene, etc.). In addition, it has been confirmed that hydrated salts can be used to plasticize other polysaccharides, such as starch, pullulan, etc. (Hirase, Nakagawa, Kubo, & Takahara, 2007; Kubo, 2007; Kubo & Takahara, 2007).

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