Preparation of cellulose–chitosan blend film using chloral/dimethylformamide

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Cellulose–chitosan blend films with varied mixing ratios (0–100%) were prepared by dissolving the polymers in chloral/dimethylformamide followed by casting onto glass plates. X-ray diffraction patterns of the films showed a gradual transition from partially crystalline cellulose to non-crystalline chitosan with increasing chitosan content. The tensile strength and Young's modulus of the blend films were greater than those calculated by adding the values of the two components according to the blend ratios. Maxima in these properties appeared at chitosan contents of 10–20%. Chitosan in the blend films showed increased resistance to extraction with acetate buffer (pH 4.5). These results suggest the occurrence of specific interactions between cellulose and chitosan molecules, probably based on the structural similarity. Solute permeability in the blend films was greater than that for pure cellulose or chitosan film.

(Keywords: cellulose; chitosan; blend)

INTRODUCTION

Chitosan, the β-1,4-linked polymer of 2-deoxy-2-amino anhydroglucose, is similar to cellulose in primary and secondary structures. The difference between the two polysaccharides is that chitosan has the deoxyamino group instead of the hydroxyl group at the C2 position of every pyranose ring. This similarity is expected to give high compatibility between these two polymers when blended in a film. Blending cellulose and chitosan is expected to be a useful method to introduce amino groups into cellulosic materials for their functionalization.

It has been reported that cellulose–chitin blends, prepared by using xanthate as a cosolvent, show improved Young's moduli and dyeing properties[1].

Cellulose–chitosan blend film was prepared by using trifluoroacetic acid as a cosolvent; the film was analysed by scanning electron microscopy, X-ray diffractometry and Raman spectroscopy[2,3]. The results suggested that cellulose and chitosan were mixed at the molecular level. Recently we found that the chloral/dimethylformamide system[4,5], a polar aprotic solvent for cellulose, also dissolves chitosan at room temperature. We report here the procedure for preparing cellulose–chitosan blend film together with its characterization through mechanical properties and performance as a dialysis membrane.

EXPERIMENTAL

Materials

A commercial chitosan (Chitosan-100L, Katokichi Co. Ltd, Kagawa, Japan) was purified by dissolving in 1% acetic acid followed by filtration through a coarse-grade glass filter and regeneration in 0.5 N sodium hydroxide solution. The precipitate was collected by filtration and washed thoroughly with water. The degree of deacetylation (96%) and the weight average degree of polymerization (480) of chitosan were determined by ^{1}H n.m.r. and size exclusion chromatography, respectively[6].

Commercial cotton was used as a cellulose sample. The viscosity average degree of polymerization of cellulose, determined by cupriethylenediamine solution, was about 1680[7].

Dissolving test of chitosan

In order to choose appropriate solvents having sufficient dissolving power for chitosan when mixed with anhydrous chloral, four types of organic solvents — pyridine, dimethylformamide (DMF), dimethylacetoamide (DMAc), and dimethyl sulfoxide (DMSO) — were tested in the following procedure. A chitosan sample (50 mg) was dispersed and swollen in 10 ml of one of the solvents and 0.21–0.83 ml of anhydrous chloral (3–12 mol per glycoside unit) was added. This chitosan–solvent–chloral mixture was occasionally shaken at room temperature or at 70°C. Chitosan required more than 3 mol of anhydrous chloral per glycoside unit for complete dissolution.

Dissolution and blending of cellulose and chitosan

Since the chloral/DMF system is known to be the most effective solvent for cellulose[8], this system was chosen as a cosolvent for a cellulose/chitosan blend from various kinds of solvents. Cellulose was dissolved in a chloral/DMF solution with a small amount of pyridine as reaction accelerator[8]: 5 g of cellulose was immersed in 222 ml of DMF, and 15.2 ml of chloral (5 mol per glycoside unit) was added to the mixture. A 12.2 ml portion of pyridine was added to facilitate dissolution of cellulose[4,8,9]. The mixture was stirred at 60°C until cellulose dissolved to give a transparent solution.

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Chitosan was dissolved in chloral/DMF as follows: 5 g of chitosan was dispersed in 235 ml of DMF, and 15.2 ml of chloral was added dropwise under continuous and vigorous stirring. Spontaneous and rapid gelation occurred followed by formation of a yellow viscous solution after several hours. The addition of pyridine was omitted because chitosan was readily dissolved in the solvent by prolonged stirring.

The separately prepared cellulose and chitosan solutions were blended at room temperature in the desired proportion, so that the chitosan content in the mixed solutions ranged from 10 to 75%. This mixed solution could be stored at room temperature for at least 4 weeks without any gelation or precipitation.

Preparation of films

The mixed solution was cast onto a glass plate, after stirring overnight. The film was formed by evaporating the solvent *in vacuo* at 130°C. The dried film on the plate was soaked in 0.5 N sodium hydroxide solution for 1 day at room temperature to remove the remaining chemicals. The wet film was washed thoroughly with water. The obtained film was spread and placed between a Teflon plate and a filter paper; it was dried and conditioned at 20°C and 65% relative humidity (r.h.). The thickness of the films was 12–15 μm, and density was 0.9–1.3 g cm^{-3}.

Analyses

Infra-red spectra of the blend films were obtained using a Shimadzu IR-435 spectrometer.

X-Ray diffraction patterns of pelletized samples were recorded on a Jeol JDX-5B X-ray diffractometer equipped with a reflection-type goniometer, using Ni-filtered CuKα radiation (wavelength, 1.54 Å).

Tensile mechanical properties of the films were measured with a Tensilon UTM-III-100 (Toyo Baldwin Co.) at 20°C and 65% r.h. All samples were cut into pieces 5 mm × 10 cm. Testing conditions were: 20 kgf load cell, elongation speed of 10 mm min^{-1}, and span length of 60 mm. The thickness of all samples was measured with a micrometer. Static Young's modulus was calculated from the initial slope of the load–elongation curves. All reported values are averages of at least eight runs.

The surface of the blend film was examined by a Hitachi S4000 scanning electron microscope at 10 kV by coating the specimen with platinum.

Permeability measurement

The film was clamped between a pair of flanged glass cylinders (*Figure 1*). On each side of the membrane the cylinders were filled with 25 ml of distilled water which could be stirred continuously by a magnetic stirrer.

A certain amount of a testing solution was added to one side (I) of the membrane to start the measurement. The subsequent change in the probe concentration of the other side (II) was determined by continuously recirculating the solution through a differential refractometer (Waters R-403). The probe solutes are summarized in *Table 1*. The area of membrane contacting the liquid was 3.14 cm^2. This measurement was carried out at 25°C.

Stability of blend film under acidic conditions

A piece of film specimen (0.3 g) was immersed in 100 ml of 0.1 M acetate buffer (pH 4.5) and the mixture was shaken for 24 h at room temperature. The remaining film was collected on a glass filter, thoroughly washed with water, and weighed to determine the amount of chitosan extracted.

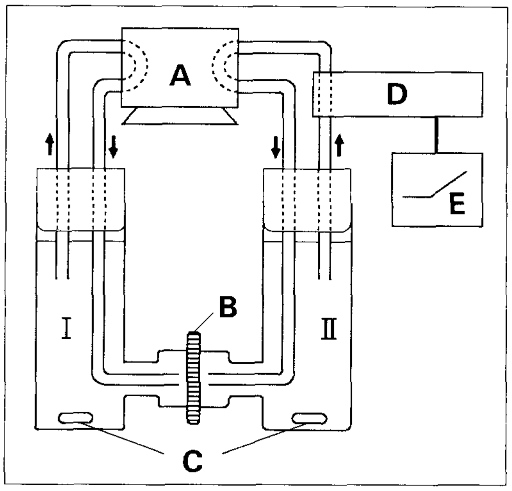

Figure 1 Dialysis testing apparatus for cellulose–chitosan blend films. I, Probe solution; II, distilled water. A, Peristaltic pump; B, membrane; C, magnetic stirrer bar; D, RI detector; E, recorder

Table 1 Probe solute used for permeability measurement of blend films

Solute	Molecular weight	Concentration
Urea	60.06	0.01 mol l^{-1}
Creatinine	113.12	0.001 mol l^{-1}
Maltose	342.3	0.01 mol l^{-1}
PEG 600[a]	600	0.25% (w/w)
Vitamin B_{12}	1355	0.001 mol l^{-1}
PEG 4000[a]	3000	0.25% (w/w)

[a] PEG, poly(ethylene glycol)

RESULTS AND DISCUSSION

Dissolution of chitosan

According to the procedure described above, chitosan could be successfully dissolved in the chloral solvent system containing DMF, DMAc or DMSO at room temperature within 2–5 h of immersion. The dissolution of chitosan proceeded in two stages.

In the first stage, gelation occurred as soon as the chloral was added to the chitosan suspension. Based on consideration about reactivity of chloral and amines in this solvent system, this stage is considered to correspond to the formation of a Schiff base at amino groups of the chitosan. This reaction would promote strong swelling of suspended chitosan particles, causing the gelation.

In the second stage, this gel-like mass was gradually converted, by continuous stirring, into a viscous, yellow liquid. In the case of dissolution of cellulose in this solvent, it is known that the formation of hemiacetal between chloral and hydroxyl groups is the driving force of dissolution[8,10]. Therefore, the same process of hemiacetal formation is likely to take place for chitosan, resulting in uniform solubilization.

Chitosan could be regenerated from this solution by pouring it into water or acetone. The i.r. spectrum of this regenerated chitosan showed a peak of C–Cl stretching at around 780 cm^{-1}. The hemiacetals formed between chloral and hydroxyl groups of cellulose are known to be unstable to aqueous solutions or alcohols; this C–Cl absorption can be ascribed to the Schiff base group formed between chloral and the amino group of chitosan. As expected from the behaviour of the Schiff base, this absorption disappeared after soaking the material in weak alkali overnight.

Properties of blend films

The cellulose, chitosan and their blend films prepared from the chloral/DMF system were all transparent and flexible without softening agents. The moisture content of the film (dry base) was 16–21% at 20°C and 65% r.h. The high flexibility of the films can be ascribed to this higher than usual moisture content for regenerated cellulose films.

Figure 2 shows X-ray diffraction patterns of the blend films. The 100% cellulose shows the diffraction pattern of partially crystalline cellulose II, whereas chitosan is completely amorphous. The patterns show a gradual transition from partially crystalline cellulose to non-crystalline chitosan with increasing chitosan content. The patterns of blend films are close to those expected from linear combination of the constituent materials.

Although the blend films were treated with 0.5 N sodium hydroxide solution to remove the Schiff base of the amino groups, the i.r. spectra (not shown) of the blend films showed that small amounts of chloral remained, unlike the case of regenerated chitosan described above.

Figure 3 shows the dependence of mechanical properties of the blend films on the blend ratios. The films had tensile strengths of 25–45 MPa and Young's moduli of 1.1–2.6 GPa. These values are of the same orders as those of commercial regenerated cellulose films. Both tensile strength and Young's modulus are remarkably greater than the values expected from additivity of properties in the entire range of chitosan content. In particular, both quantities have maxima at a chitosan content of 10–20%.

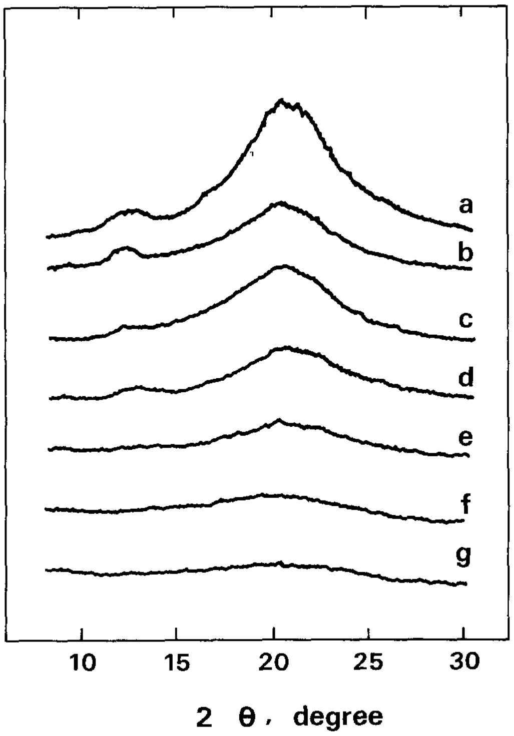

Figure 2 X-Ray diffractograms of cellulose–chitosan blend films. Chitosan content (w/w) of the films: (a) 0%; (b) 10%; (c) 20%; (d) 30%; (e) 50%; (f) 75%; (g) 100%

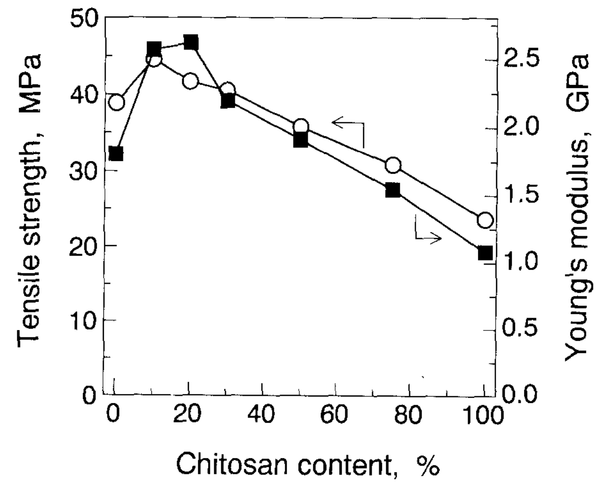

Figure 3 Mechanical properties of cellulose–chitosan blend films; ○, tensile strength; ■, Young's modulus

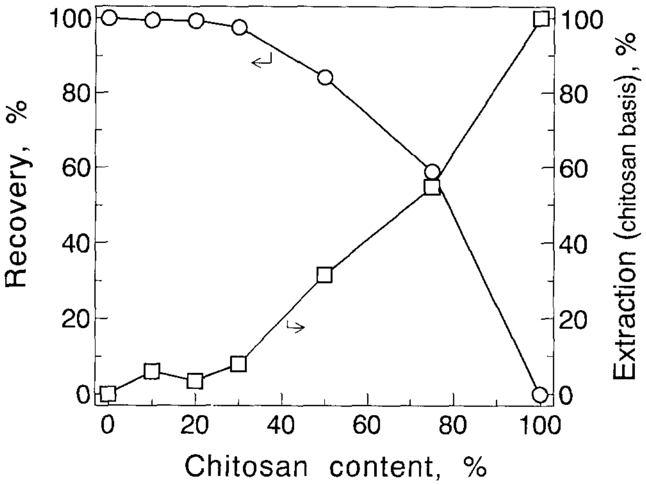

Figure 4 Extraction of chitosan from blend films with acetate buffer (pH 4.5). ○, Percentage of insoluble material to the starting film; □, percentage of extracted chitosan to chitosan in the blend film

This anomalous enhancement of mechanical properties suggests the occurrence of specific interaction between cellulose and chitosan molecules based on their structural similarity. The improvement of tensile strength and static Young's modulus of the blend films at around 10–20% chitosan content seems to be derived from the presence of interaction between cellulose and chitosan molecules in the films.

Because many end-uses of polymeric films involve contact with water, the resistance of the blend film to aqueous treatments is important. Since chitosan is readily soluble in acidic solutions (pH 4.5 acetate buffer), the behaviour of chitosan in the blend film obtained here is of interest. Under the tested acidic condition, the blend film retained its shape up to 50% chitosan film, the 75% chitosan film disintegrated into small pieces, and the 100% chitosan film dissolved completely.

Figure 4 shows the extraction behaviour of chitosan. Apparently the chitosan in the blend film is remarkably resistant to acidic extraction. The ratio of the extracted

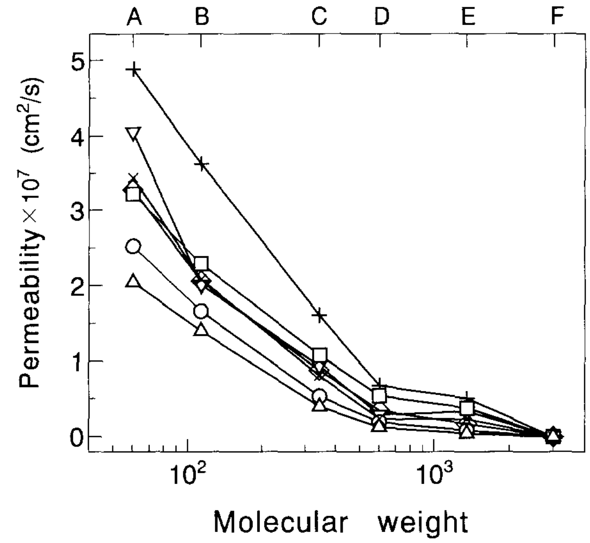

Figure 5 Solute permeability of cellulose–chitosan blend films. Chitosan content: ○, 0%; +, 10%; ▽, 20%; □, 30%; ◇, 50%; ×, 75%; △, 100%. A–F indicate molecular weights of urea (A), creatinine (B), maltose (C), PEG 600 (D), vitamin B_{12} (E), and PEG 4000 (F)

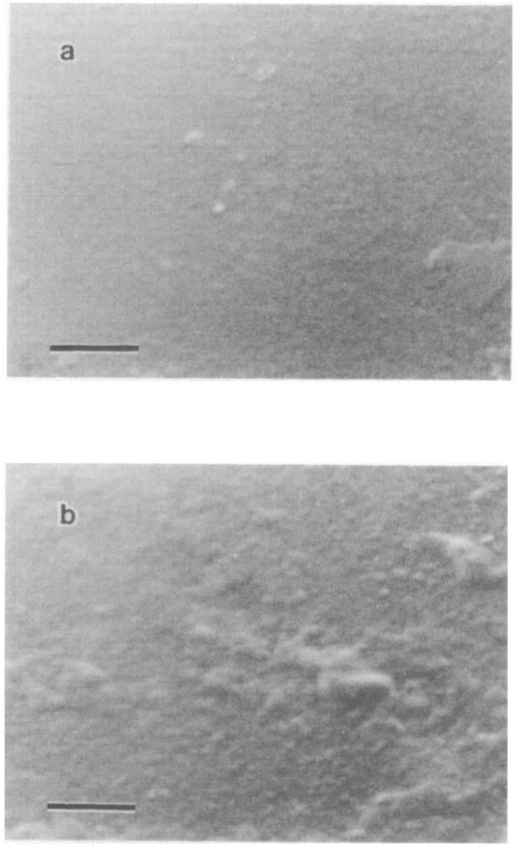

Figure 6 Scanning electron micrographs of cellulose–chitosan blend films (50% chitosan content). (a) Original blend film; (b) acidic buffer-treated film. Scale bars = 1 μm

amount to the initial amount is as low as 10% up to a chitosan content of 30%, and gradually increases to 100% for pure chitosan. In the range of less than 30% chitosan content, chitosan molecules seem to be closely embedded in the cellulose matrix. These results show that this method of blending gives the possibility of immobilizing chitosan for use under acidic conditions without reinforcing chemical treatments.

Permeability of blend films

Figure 5 shows the molecular weight (*MW*) dependence of permeation rates of the blend films. The cut-off *MW* for ethylene glycol was below 3000 for all films tested. The permeation rates of the blend films were greater than those of pure cellulose or chitosan films. A maximum in permeability was observed at a chitosan content of 10%. This composition agrees with that giving the maximum improvement in tensile properties.

These results suggest that cellulose and chitosan molecules are highly compatible with each other, and blending of chitosan is effective in preventing the formation of cellulose crystallites during the film formation process. Such a blend structure is considered to provide a more amorphous and homogeneous structure, which results in improved mechanical properties and higher permeability.

Scanning electron microscopy

Figure 6a shows the scanning electron micrograph of the surface of the blend film containing 50% chitosan (this specimen has been re-swollen in water and freeze-dried in order to be comparable with the acetate buffer-treated sample, see below). The surface is extremely smooth and gives no indication of heterogeneity. *Figure 6b* shows the same film as in *Figure 6a* but after treatment with the acetate buffer (pH 4.5) followed by freeze-drying. While about 30% of chitosan (chitosan base) has been extracted from the starting material, the surface shows no apparent voids or cracks suggestive of domain-like structures; however, many parts of the surface are covered with irregular-shaped protrusions, which are likely to be formed through shrinkage of the matrix after removal of extractable chitosan. These observations are consistent with the above-stated features, indicating mixing of chitosan and cellulose at the molecular level.

Comparison with trifluoroacetic acid-based blend film

The properties of the blend films prepared here are largely similar to those of cellulose–chitosan blends cast from trifluoroacetic acid (TFA) solution[3]. The present solvent of chloral/DMF, however, has clear advantages over the TFA method in terms of easier handling of the solvent and faster dissolution of the polymers.

CONCLUSION

Blending cellulose with chitosan leads to novel and desirable characteristics, including improved mechanical properties, increased stability of chitosan, and higher solute permeability. This method of blending is also useful in preparing cellulosic materials containing immobilized amino groups. Such materials should have both the strength of cellulose and the functionality of chitosan.

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