

Characterization of Cellulose–Chitosan Blend Films

MAKOTO HASEGAWA,¹ AKIRA ISOGAI,^{1*} FUMIHIKO ONABE,¹ MAKOTO USUDA,¹ and RAJAI H. ATALLA²

¹Department of Forest Products, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan;

²Forest Products Laboratory, Forest Service, USDA, Madison, Wisconsin 53715-2398

SYNOPSIS

Interactions between cellulose and chitosan molecules in cellulose–chitosan blend films, prepared using trifluoroacetic acid as a cosolvent for the two polysaccharides, were studied by X-ray diffraction and Raman analyses and by measurements of mechanical properties of the blend films. Crystallinity of cellulose in the blend films decreased with an increase in chitosan content. The blend films had tensile strengths of 45–100 MPa and Young's moduli of 2–7.5 GPa in dry states. These values had the maximum around 30% chitosan content in the blend films. These results suggested the presence of interactions between cellulose, chitosan, and water molecules in the films. However, Raman analysis suggested that cellulose and chitosan molecules in the blend films seemed to have the same secondary structures as those in 100% cellulose and 100% chitosan films, respectively. Thus, these results indicate the presence of interactions in the interfacial region between small domains of cellulose and chitosan. The presence of chitosan molecules may lead to decrease in the domain size of cellulose, and to increase in the interfacial region between cellulose and chitosan domains.

INTRODUCTION

Chitosan consists of 2-deoxy-2-amino anhydroglucose residues, and has the same β -1,4 glycosidic bonds as cellulose. Since chitosan is a biodegradable polysaccharide having amine groups, many papers have recently been published concerning utilization of chitosan as functionalized polysaccharides. One method to introduce amine groups into cellulosic materials is the polymer blend of chitosan and cellulose by means of cosolvents for the two polysaccharides. In this case, chitosan is expected to act as a material for supplying amine groups, and cellulose is expected to act as a material for supporting chitosan to have sufficient mechanical strength.

Miya et al. reported the preparation of blend films of poly(vinyl alcohol) and chitosan, and their application to dialysis membrane.¹ The blend films showed the maximum values of mechanical strength at 15–30% chitosan content. This observation together with the results of Raman and electron mi-

croscopic analyses suggested that poly(vinyl alcohol) and chitosan molecules had some intermolecular interactions in the blend films. Also in the case of cellulose–chitosan blends, good compatibility is expected because of the structural similarity between the two polysaccharides, and furthermore the presence of cellulose may improve film properties for dialysis membrane.

In the previous paper,² blend films of cellulose and chitosan were prepared using trifluoroacetic acid as a cosolvent for the two polysaccharides, and were characterized by X-ray diffraction and scanning electron microscopic analyses. The results indicated that molecules of the two polysaccharides were homogeneously mixed in the blend films.

In this study, therefore, characterization of the blend films of cellulose and chitosan were further studied in detail in terms of compatibility of the two polysaccharides. Differential scanning calorimetric analysis is one of the convenient methods for evaluating compatibility of polymers in blends. Cellulose and chitosan, however, have no clear glass-transition temperature (T_g), and hence the compatibility or interactions between cellulose and chitosan molecules in the blend films were studied in terms of the relationship between chitosan content and either X-

* To whom correspondence should be addressed.

ray diffraction patterns, Raman spectra, or mechanical properties, in this study.

EXPERIMENTAL

Materials

A commercial chitosan (PSH, Yaizu Suisan Kagaku Co. Ltd., Yaizu, Shizuoka, Japan) was purified by dissolving in 5% acetic acid followed by regenerating into 0.5N NaOH solution through a glass filter. The precipitate was collected by filtration, and washed sufficiently with water. The purified chitosan was obtained by freeze drying, and had a degree of deacetylation more than 80%. The weight average degree of polymerization (DP_w) of chitosan was about 500.³ Commercially available cotton (loose fiber), whose DP_w was 1700 (the Cuen method),⁴ was used as a cellulose sample. All chemicals used were of special grade.

Preparation of Films

According to the previous paper,² cellulose and chitosan (total weight = 0.5 g) were placed in a Erlenmeyer flask (50 mL), and trifluoroacetic acid (20–25 mL) was added to the flask equipped with an universal stopper. The suspension turned to a clear solution within 2 days at room temperature without stirring. The weight ratios of cellulose and chitosan were controlled to 10 : 0, 9 : 1, 8 : 2, 7 : 3, 5 : 5, and 0 : 10. After a clear solution was obtained, acetic acid was added to the solution for dilution in order to control the viscosity suitable for casting (ca. 0.8–1.2 wt %); the viscosity control was performed to obtain dry films having thickness within the range from 15 to 25 μm . The solution was then cast on a glass plate, and the plate was kept in a hood more than 2 days for removing the solvents. The dry film with the glass plate was soaked in 1N NaOH solution for 1 day at room temperature, and then the wet film, which was peeled off spontaneously from the glass plate during the alkali soaking, was washed sufficiently with water. The wet film thus obtained was placed between a metal plate and a filter paper, according to the TAPPI test method for drying handsheets of pulp,⁵ and was dried and conditioned at 20°C and 65% relative humidity for more than 1 day.

Thermal Treatment

The films were heated in an oven at 70 and 115°C for 1 h, and then conditioned at 20°C and 65% relative humidity for more than 1 day.

Analyses

Moisture content was determined according to the following equation:

$$\text{moisture content (\%)} = \frac{W_{\text{con}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where W_{con} is the weight of the film, which was conditioned at 25°C and 65% relative humidity for more than 1 day, and W_{dry} is the weight of the film after being dried at 105°C for 3 h.

Infrared spectra of neat films were obtained using a Shimadzu IR-435. Deacetylation of chitosan was calculated from nitrogen content and IR spectra.^{6,7}

X-ray diffraction patterns of pellet samples were recorded on a JEOL JDX-5B diffractometer equipped with a reflection type goniometer and the pulse-height-discriminator system, using Ni-filtered CuK_α radiation. Irradiation conditions were 30 kV and 25 mA, and the scanning rate was 1°/min of the diffraction angle 2θ .

Raman spectra were acquired with a Jobin Yvon Ramanor spectrometer and an HG 2S monochromator system, using the 514.5 nm line of an argon laser operated, at 10 mW, as the exciting source. Data were accumulated 10–15 times.

Tensilon UTM-III-100 (Toyo Baldwin Co. Ltd.) was used to obtain strain–stress curves of the samples. The specimen size of the films was 5 × 80 mm, and 10 specimens were subjected to the test for one sample. Testing conditions were: 20 kg load cell, measuring speed of 10 mm/min, and 25 mm span length. Film thickness was measured by using a thickness tester, according to a TAPPI test methods.⁸

Static Young's moduli were calculated from the initial slope of the above stress–strain curves. Dynamic Young's moduli were recorded using a dynamic modulus tester (PPM-5R, H. M. Morgan Co., Ltd., USA).

RESULTS AND DISCUSSION

General Properties of Blend Films

As described in the previous paper,² TFA can be used to dissolve both cellulose and chitosan. Although cellulose and chitosan required different time for complete dissolution in TFA, clear and apparently homogeneous solutions of cellulose and chitosan in TFA were obtained within 2–3 days. After both cellulose and chitosan were dissolved in TFA, acetic acid or formic acid can be freely added to the solution without regenerating the polysaccharides.

This addition of acetic acid was useful to control viscosity of the solution for casting. As described in Experimental, TFA and acetic acid present in the dry cast films were removed by soaking them in 1N NaOH solution. The blend films of cellulose and chitosan thus obtained were transparent, and had sufficient flexibility and strength without the addition of plasticizers into the films. Density of the films was 1.1–1.4 g/cm³. As reported in the previous paper,² DP_v of cotton cellulose was decreased during the dissolution and regeneration procedure, and regenerated films of cotton cellulose had DP_v of about 600. DP_w values of chitosan were about 500 even after the film preparation procedure.

IR spectra of the blend films showed that TFA and acetic acid were completely removed from the films by the alkali treatment and that the absorption due to amine groups at 1580 cm⁻¹ increased with chitosan content in the films.⁶ No difference of IR spectra between the original films and those after the thermal treatments was observed.

Table I shows moisture content of cellulose–chitosan blend films. The films had 12–19% moisture content after being conditioned, and the moisture content of films increased with chitosan content. The flexibility of the blend films seems to be ascribed to this higher moisture content. The thermal treatments resulted in a decrease in moisture content, and this observation must be explained in terms of dewatering in an accessible region to moisture, together with hydrogen-bond formation of hydroxyl groups of polysaccharides molecules in the region.

X-Ray Analysis of Blend Films

X-ray diffraction patterns of the blend films are shown in Figure 1. Cellulose had crystal structure of cellulose II, and chitosan films had the pattern reported by Sakurai et al.,⁹ respectively. Although

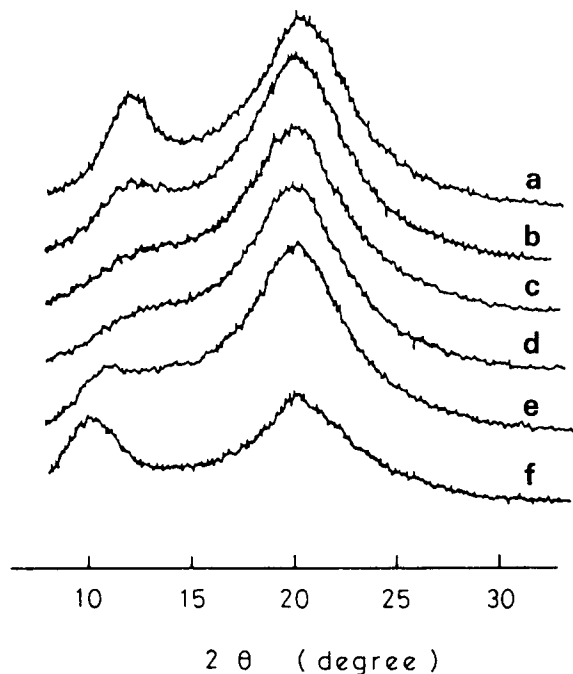


Figure 1 X-ray diffraction patterns of cellulose–chitosan blend films. Cellulose : chitosan: (a) 10 : 0; (b) 9 : 1; (c) 8 : 2; (d) 7 : 3; (e) 5 : 5; (f) 0 : 10.

no peaks other than those of cellulose and chitosan themselves were detected in the patterns of blend films, crystallinity of these films was lower than that of the 100% cellulose film.

If cellulose and chitosan have low compatibility in the blend films, each polysaccharide has its own crystal region in the blend films, and X-ray diffraction patterns are expressed as simply mixed patterns of cellulose and chitosan with the same ratios as those for blending. Figure 2 shows calculated curves of X-ray diffraction patterns of blend films, on the assumption that the crystal structures of cellulose and chitosan are present independently in the films. Cauchy's function was used in this study for peak separation.¹⁰

$$I(x) = ax + b + \sum_{i=1}^n I_i / \{1 + k_i^2(x - x_i)^2\} \quad (2)$$

where $I(x)$ is the total intensity at $2\theta = x$, and I_i , k_i and x_i are the intensity, peak broadening factor, and peak position, respectively, of the peak type i . First, the X-ray diffraction patterns of the 100% cellulose and 100% chitosan films were expressed as $I(x)_{\text{cellulose}}$ and $I(x)_{\text{chitosan}}$, respectively, and then the pattern of the blend film containing 30% chitosan, for example, was obtained from

Table I Effect of Dry-Thermal Treatment on Moisture Content of Cellulose–Chitosan Blend Films

Chitosan Content in Blend Film (%)	Thermal Treatment (°C)		
	20	70	115
0	12.4	9.8	9.7
10	12.0	—	—
20	13.2	—	—
30	13.7	—	10.6
50	14.0	10.7	10.4
100	19.1	15.8	13.7

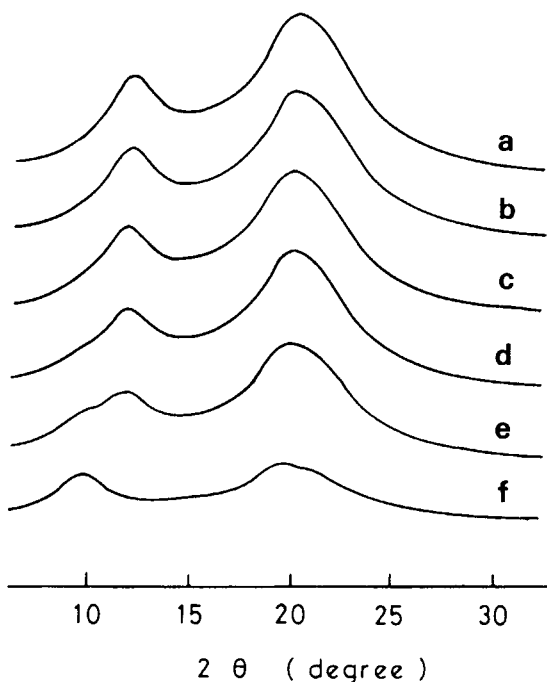


Figure 2 Calculated X-ray diffraction patterns of cellulose-chitosan blends. Obtained by peak separation method from X-ray diffraction patterns of cellulose and chitosan, using Cauchy's functions described in the text. Cellulose : chitosan: (a) 10 : 0; (b) 9 : 1; (c) 8 : 2; (d) 7 : 3; (e) 5 : 5; (f) 0 : 10.

$$I(x)_{\text{blend}30} = 0.7 \times I(x)_{\text{cellulose}} + 0.3 \times I(x)_{\text{chitosan}} \quad (3)$$

In comparison with the calculated patterns in Figure 2, the actual X-ray diffraction patterns in Figure 1 showed clearly lower crystallinity. Especially the appearance of $1\bar{1}0$ peak of cellulose II around $2\theta = 12.5^\circ$ was prevented even by mixing 10% chitosan. These results suggest that the presence of chitosan in the film prevents the crystallization of the cellulose molecules to cellulose II: Some interactions between cellulose and chitosan molecules must be present in the films.

Figure 3 shows X-ray diffraction patterns of cellulose-chitosan blend films heated at 70 and 115°C for 1 h. Generally, thermal or annealing treatments bring about increase in crystallinity of cellulose.¹¹ However, crystallinity of cellulose II in cellulose and cellulose-chitosan films slightly decreased with increasing temperature, although the intensity of 100 peak ($2\theta = 10^\circ$) in the chitosan film increased. As described in the former section, the thermal treatments brought about decrease in moisture content of the blend films, indicating that some hydrogen-

bond formation in the films. This hydrogen-bond formation, however, did not extend to crystallization in the blend films.

Raman Analysis of Blend Films

The compatibility between cellulose and chitosan in the blend films were further examined by Raman

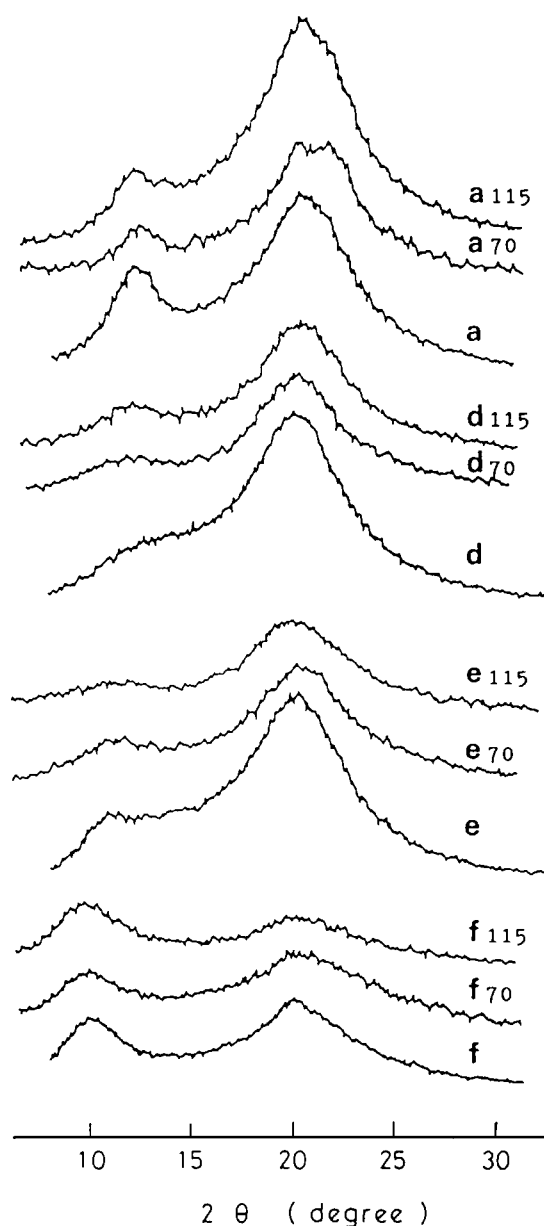


Figure 3 X-ray diffraction patterns of cellulose-chitosan blend films heated at 70 and 115°C for 1 h. Letters and numbers correspond to those of the samples in Figure 1 and the temperature of thermal treatments, respectively. Letters without number were samples without thermal treatments.

spectroscopy. Figure 4 shows Raman spectra of cellulose, cellulose-chitosan blend, and chitosan films without thermal treatments. Cellulose and chitosan had Raman spectra similar to each other, probably because molecules of the two polysaccharides had

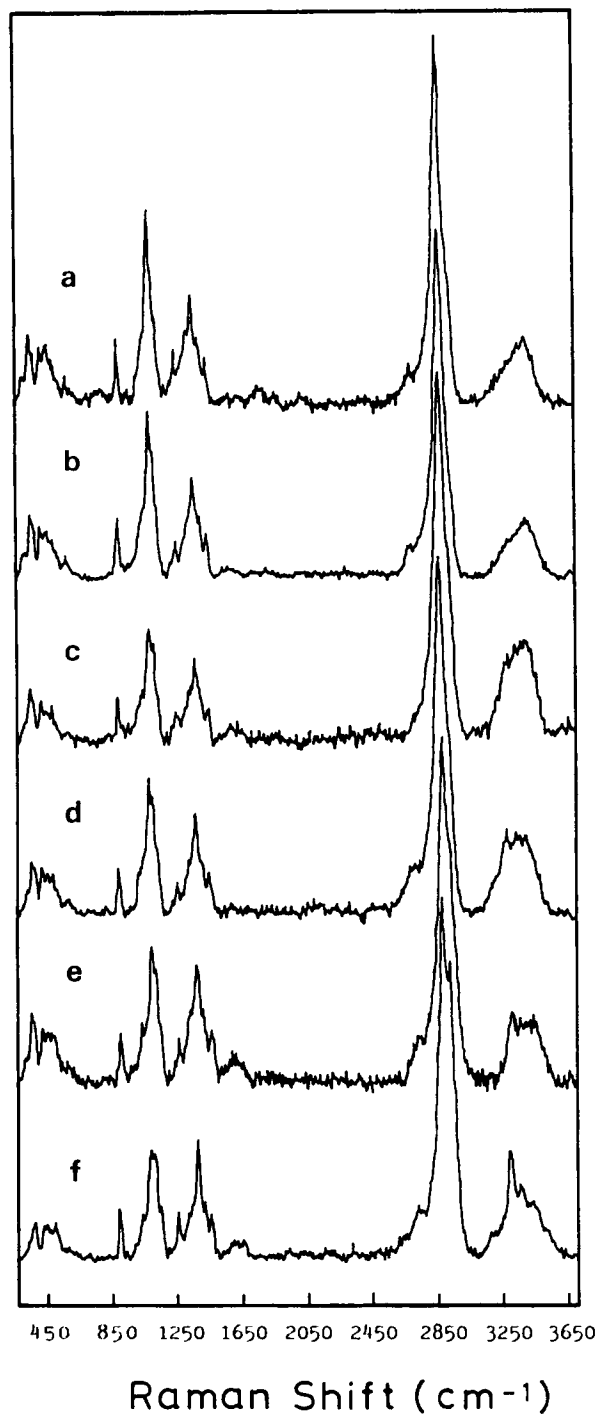


Figure 4 Raman spectra of cellulose-chitosan blend films. Cellulose : chitosan: (a) 10 : 0; (b) 9 : 1; (c) 8 : 2; (d) 7 : 3; (e) 5 : 5; (f) 0 : 10.

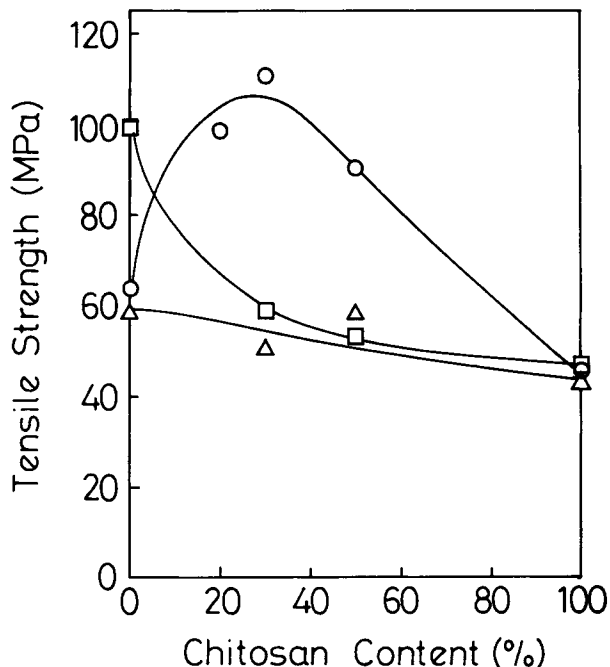


Figure 5 Tensile strength of cellulose-chitosan blend films: (O) conditioned samples; (Δ) conditioned samples after thermal treatment at 70°C for 1 h; (□) conditioned samples after thermal treatment at 115°C for 1 h.

linear structures due to β -1,4 glycosidic bonds. In comparison with Raman spectra of highly crystalline celluloses,¹² the samples in Figure 4 had broad peaks due to low crystallinity, and this was consistent with the results of X-ray diffraction analysis, as described in the previous section. Differences between Raman spectra of cellulose and chitosan were: (1) the presence of peaks due to N—H around 3300–3350 cm^{-1} for chitosan, and (2) detailed patterns from 300 to 550 cm^{-1} .

Atalla reported that Raman spectra with the range from 300 to 550 cm^{-1} have information concerning secondary structures of solid-state polysaccharides.¹³ If cellulose and chitosan have interactions in the blend films such as hydrogen bond formation between cellulose and chitosan molecules, Raman patterns of the blend films may have new peaks different from those of the 100% cellulose and 100% chitosan films. However, as shown in Figure 4, Raman patterns of the blend films had no peaks other than those of the 100% cellulose and 100% chitosan films, and the patterns of the blend films were almost the same as those of simply mixed patterns of cellulose and chitosan with blending ratios. This result indicates that most of cellulose and chitosan molecules in the blend films have the same secondary structures as those in their own films, and

that most of cellulose and chitosan molecules may not have intermolecular hydrogen bonds between the two kinds of polysaccharides. The samples heated at 70°C had Raman spectra almost identical to those of samples without thermal treatment. The samples heated at 115°C had strong fluorescence in the spectra, and hence it was difficult to obtain good Raman spectra.

Mechanical Properties of Blend Films

Figure 5 shows tensile strength of conditioned films. The films without thermal treatments had a tensile strength of 45–110 MPa, and the maximum value was observed at 30% chitosan content. The remarkable increase in tensile strength of this blend film indicates the presence of some interaction between cellulose and chitosan molecules in the film.

On the other hand, the heated samples had the maximum tensile strength at 100% cellulose, and the values decreased with chitosan content. This observation suggests that the interaction between cellulose and chitosan molecules present in the blend films without the thermal treatment may no longer be present in the heated samples.

Figure 6 shows elongation of the films at the breaking point of tensile strength measurements. These elongation patterns corresponded well to the results in Figure 5.

Young's moduli of the samples with and without thermal treatments were shown in Figure 7. Dy-

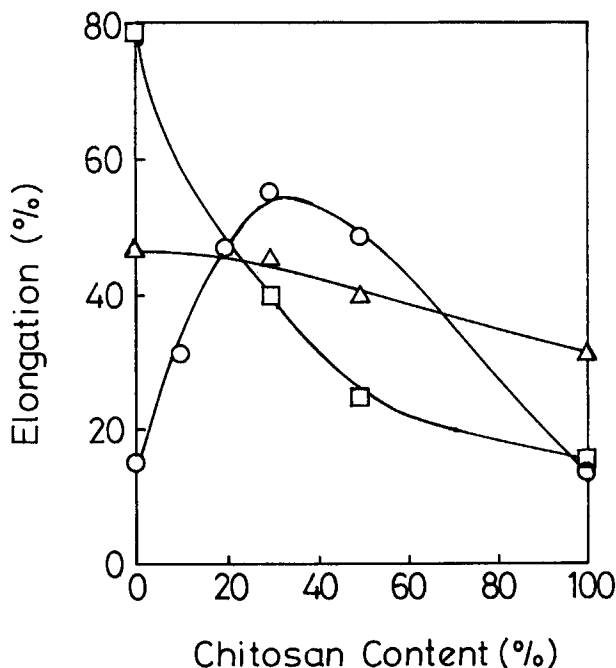


Figure 6 Elongation (%) at breaking point of cellulose-chitosan blend films. See Figure 5 for the symbols.

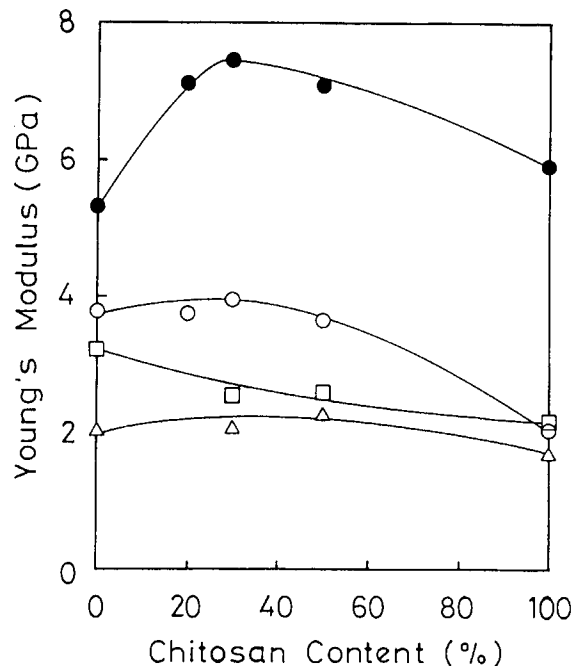


Figure 7 Relationship between Young's modulus and chitosan content of cellulose-chitosan blend films: (O) static Young's modulus; (●) dynamic Young's modulus; (Δ) static Young's modulus of samples heated at 70°C for 1 h; (□) static Young's modulus of samples heated at 115°C for 1 h.

amic Young's moduli of the films were 5.3–7.5 GPa, and the maximum value was observed at 30% chitosan content. On the other hand, static Young's moduli of the films were 2–4 GPa, and the relation between the maximum value and chitosan content in the films was not so clear as that obtained by dynamic Young's moduli measurement. Young's moduli of the heated samples were lower than those of samples without thermal treatments.

These mechanical properties of the blend films without the thermal treatment suggest that the improvement of tensile strength of the blend films around 30% chitosan content is attributed to the improvement of plasticity of the films and that this improvement may be derived from the presence of interactions between cellulose, chitosan, and water molecules in the films. Thermal treatments seem, in turn, to destroy the interactions, and bring about the decrease in both tensile strength and Young's moduli of the films.

Interactions between Cellulose and Chitosan in Blend Films

On the basis of the above results, interactions between cellulose and chitosan molecules in the blend films were examined. X-ray diffraction patterns and

mechanical properties of the blend films indicated the presence of interactions between cellulose, chitosan, and water molecules in the films. Raman spectra of the blend films, on the other hand, showed that most of cellulose and chitosan molecules in the blend films had the same secondary structures as those in 100% cellulose and 100% chitosan films, respectively. These observations suggest that interactions between cellulose, chitosan, and water molecules may be present in the blend films but not predominantly: Cellulose and chitosan molecules may still have their own domains much smaller than those of 100% cellulose and 100% chitosan films, and interactions may be present in the interfacial region between the two domains. Thus the presence of chitosan molecules may lead to decrease in the domain size of cellulose, and increase in the interfacial region between the domains of cellulose and chitosan. Thermal treatments of the films may destroy the interaction of the interfacial region, resulting in the decrease in mechanical strength.

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