

Chemical Crosslinking of Hydroxypropyl Cellulose and Chitosan Blends

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SYNOPSIS

Two liquid crystal forming polysaccharides, hydroxypropyl cellulose and chitosan, were blended in aqueous acetic acid solutions and were crosslinked with dialdehydes (glyoxal and glutaraldehyde) as crosslinker and hydrochloric acid as catalyzer. The crosslinkability, morphology, solubility, and tensile properties of the crosslinked blend films are determined and the dependence of those properties on the blend composition and on crosslinker species are discussed. The crosslinked blend films cast from the aqueous acetic acid solutions were amorphous. The solubility, Young's modulus, and tensile strength of the crosslinked blend films greatly depended on blend composition; those properties appeared to exhibit a maximum and a minimum around given blend compositions. The solubility for the crosslinked blend film cast from glyoxal system was greater than that from glutaraldehyde one. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

We have investigated the chemical crosslinking of cholesteric liquid crystal forming hydroxypropyl cellulose (HPC) with dialdehydes^{1,2} and with other crosslinkers.³⁻⁶ Another polysaccharide, chitosan, has also formed a liquid crystal^{7,8} and has crosslinked with glutaraldehyde⁹⁻¹² and with other crosslinkers.¹³⁻¹⁵ The mechanism of crosslinking reaction with dialdehyde for each polysaccharide has been proposed.^{1,11} The chemical structure of the chitosan backbone is very similar to that of HPC.¹⁶ Therefore, we expect that HPC is miscible with chitosan. When the blend system of HPC and chitosan in a cosolvent containing glutaraldehyde was cast under suitable conditions, the blend could form an interpenetrating polymer network (IPN). Furthermore, the blend offers the primary amino group into the cellulose derivatives, without chemical modifications. The physical introduction of the amino group into the cellulosic materials results in exciting applications. The blendings of

chitosan with cellulose^{17,18} and other human-made polymers^{11,12,19} have tried to characterize those specific properties. Nishio et al.²⁰⁻²² have investigated the properties of composites of cellulose and human-made polymers.

In this study, the blend of HPC with chitosan was tried by using aqueous acetic acid as a cosolvent, and then the chemical crosslinking of the blend was tried by casting the ternary system with two kinds of dialdehyde crosslinker and a acid catalyzer. The crosslinkability was ascertained by solubility measurement of the cast films. In this study, the crosslinkability is defined as the capability of forming a crosslinked network. The morphology of resultant crosslinked solid films as a function of mainly blend composition was observed by optical techniques such as polarized microscopy (POM) and circular dichroism (CD). The swelling behavior and tensile properties of the crosslinked blend films were also determined.

One of the major problems in this study was the limited solubility of chitosan in our solvent. Consequently, the crosslinked chitosan films retaining liquid crystalline order were difficult to prepare in this study.

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EXPERIMENTAL

Samples

Commercial-grade HPC (Tokyo Kasei Kogyo Co. Ltd.) was used. The molecular weights (\bar{M}_w and \bar{M}_n) and molar substitution of HPC were 11.7×10^4 and 5.29×10^4 and 4.25, respectively.¹⁻⁶ Chitosan was purchased from Tokyo Kasei Kogyo Co. Ltd. The molecular weight M_n of chitosan was 15.0×10^4 , by viscometry using the method of Kataoka.²³ The degree of deacetylation of chitosan was 56%. Glyoxal and glutaraldehyde (Tokyo Kasei Kogyo Co. Ltd.) were used as crosslinkers. Acetic acid and hydrochloric acid (Kanto Chemical Co. Ltd.) were used as a solvent and a catalyzer. Distilled water was prepared in our laboratory. All samples were used without further purification.

Preparation of Blend Solutions

The solubility of chitosan was considerably less than that of HPC in our conditions. Consequently, a given amount of chitosan was dissolved in a 5% aqueous acetic acid solution with stirring magnetically at room temperature. Then a given amount of HPC was blended, followed by the addition of 1% hydrochloric acid (catalyzer) and a given percentage of crosslinker, with stirring. The bubbles in the solution were removed by centrifugation (1600 rpm) for 24 h. Total polymer concentration of the solution was 1 wt %. The blend solution was stored in a refrigerator (ca. 7°C). The blend composition was expressed by the letters HPC/chitosan followed by numbers indicating the wt % of HPC and chitosan.

Preparation of Crosslinked Solid Films

The blend solution was cast on the glass plate at room temperature (ca. 20°C). The resultant film was peeled from the plate and then was vacuum dried for 24 h. The films (thickness 20–30 μm) were stored in a dessicator at room temperature.

Solubility Measurement of the Crosslinked Films

A piece (2 cm \times 2 cm) of specimen was cut from the cast films and was immersed in 5% aqueous acetic acid solution for 24 h. The solubility S was determined based on the following equation:

$$S(\%) = (W_0 - W)/W_0 \times 100 \quad (1)$$

where W_0 is an initial weight of specimen and W is a weight of specimen vacuum dried after the immersion for 24 h.

Swelling Behavior of the Crosslinked Films

The cast films subjected to solubility measurement were dried at room atmosphere and then were vacuum dried for 1 week. The dried film (weight W'_0) was immersed in 5% aqueous acetic acid solution for 24 h and then the swollen film (weight W') was weighed after the surfaces of the film were wiped with soft paper tissue. The swelling ratio B was obtained by the following equation:

$$B(\%) = (W' - W'_0)/W'_0 \times 100 \quad (2)$$

Optical Measurements of the Crosslinked Films

POM was performed by using an Olympus polarized microscope (with 150 \times magnification). CD spectra were detected with a Jasco J-40S spectropolarimeter (Japan Spectroscopic Co. Ltd.) at room temperature (ca. 20°C).

Tensile Properties of the Crosslinked Films

The properties of the films (size 3.0 cm long \times 0.3 cm wide \times 20–30 μm thick) were determined by using a Tensilon VTM-IV-500 (Toyo Baldwin Co.) at room atmosphere (ca. 20°C, 55% relative humidity [RH]). The crosshead speed was 5 mm/min. At least five measurements were performed, and the mean was obtained for the films.

RESULTS AND DISCUSSION

Crosslinkability of Each Pure Polysaccharide and of the Blend

The chemical crosslinking of chitosan and HPC greatly depended on the crosslinking conditions; especially, on the crosslinker and acid catalyzer. Table I shows the crosslinkabilities of chitosan and HPC. For chitosan, when glutaraldehyde was used as a crosslinker, the brown gel was formed and was insoluble, irrespective of the type of acid catalyzers. On the other hand, when glyoxal was used as a crosslinker, the crosslinkability of chitosan depended on the acid catalyzer; the acetic acid system formed transparent gel which was insoluble, and the hydrochloric acid system formed transparent film which dissolved. For HPC, on the contrary, the hy-

drochloric acid system could form the insoluble film and the acetic acid system could form the dissolved one, irrespective of the type of crosslinkers (glyoxal and glutaraldehyde). Our results clearly showed that both acetic acid and hydrochloric acid are required as the catalyzers for the crosslinking of chitosan/HPC blend when using dialdehydes; the crosslinking of chitosan needed no hydrochloric acid, whereas the crosslinking of HPC needed the hydrochloric acid. Figure 1 shows the solubility of crosslinked HPC film. This result showed that ca. 0.5–1% of the hydrochloric acid is enough for crosslinking the HPC. Furthermore, the crosslinkability of the blend depended on the crosslinker concentration. Figure 2 shows the solubility of the crosslinked blend film of composition 50/50 (HPC/chitosan) as a function of glyoxal concentration with 0.5% hydrochloric acid. Over the ca. 6% crosslinker concentration, the films dissolved; this means that the crosslinking needs a suitable crosslinker concentration. When the acetic acid concentration was relatively low (1%), the film dissolved. This trend was the same for the other hydrochloric acid concentrations systems

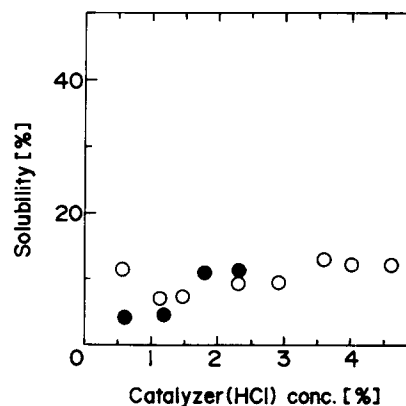


Figure 1 The dependence of solubility for crosslinked HPC film on hydrochloric acid concentration. Crosslinker: ○ glyoxal, ● glutaraldehyde.

(1%). For the glutaraldehyde system, however, the solubility of the crosslinked blend films (composition 50/50) was independent of crosslinker concentration, as shown in Figure 3. For the same system with 1.0% hydrochloric acid, the solubility behaved similarly to that shown in Figure 3, except for the higher

Table I Crosslinkability of Chitosan and HPC

Crosslinker/Conc. (%)	Solvent/Conc. (%)	Form	Color	Solubility ^a
Chitosan				
Glyoxal/1.0	Acetic acid/0.5	Gel	Transparent	X
2.0				X
3.0				X
1.0	Hydrochloric acid/0.5	Film	Transparent	○
2.0				○
3.0				○
Glutaraldehyde				
1.0	Acetic acid/0.5	Gel	Brown	X
2.0				X
3.0				X
1.0	Hydrochloric acid/0.5	Gel	Brown	X
2.0				X
3.0				X
HPC				
Glyoxal/1.0	Acetic acid/0.5	Film	Transparent	○
2.0				○
3.0				○
1.0	Hydrochloric acid/0.5	Film	Transparent	X
2.0				X
3.0				X
Glutaraldehyde				
1.0	Acetic acid/0.5	Film	Transparent	○
2.0				○
3.0				○
1.0	Hydrochloric acid/0.5	Film	Transparent	X
2.0				X
3.0				X

^a ○, soluble; ×, insoluble.

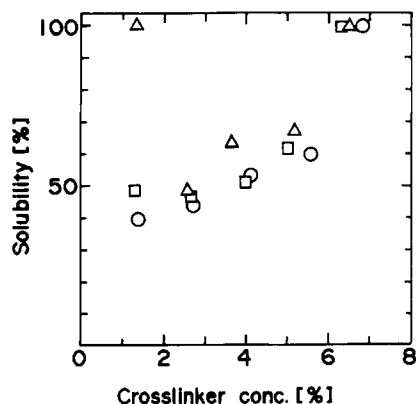


Figure 2 The dependence of solubility for crosslinked blend film (50/50) on glyoxal concentration. Hydrochloric acid concentration: 0.5%. Acetic acid concentration (%): ○ 5.0, □ 3.0, △ 1.0.

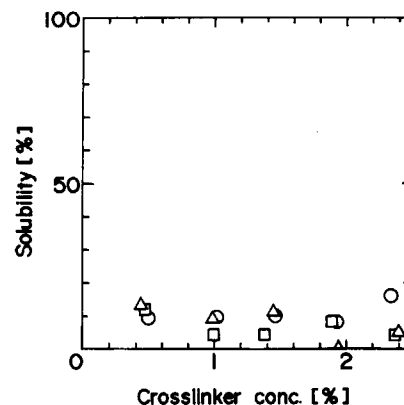


Figure 3 The dependence of solubility for crosslinked blend film (50/50) on glutaraldehyde concentration. Hydrochloric acid and acetic acid concentrations were the same as in Figure 2.

solubility (ca. 20%). With respect to the swelling ratio of crosslinked blend films with 50/50, the increase in glutaraldehyde concentration reduced the swelling ratio, as shown in Figure 4. On the other hand, the dependence of swelling behavior for crosslinked films on glyoxal concentration was not simple: The swelling ratio tended to exhibit a minimum around 3% of glyoxal concentration. The values of swelling ratio were about two to four times those for glutaraldehyde. This trend was identical with our data for pure HPC.¹

Our results clearly indicated that a suitable choice of acid catalyzer and crosslinker type and of their concentrations is required to form the crosslinked blends. Consequently, we mainly prepared the blend solution (total polymer concentration 1%) in 5% aqueous acetic acid solution with 0.5–1% hydrochloric acid and 2% glyoxal or 1% glutaraldehyde.

Morphological Observations of the Crosslinked Blend Films

There was a distinct difference in textures between crosslinked and un-crosslinked films under POM observation; the un-crosslinked films with each composition exhibited some textures that corresponded to cholesteric liquid crystalline orders, whereas the crosslinked films with each blend composition exhibited no texture. The CD spectra for the crosslinked films showed no peak, although those for the un-crosslinked films showed a negative peak. These results clearly show that the crosslinked blend films are amorphous, whereas the un-crosslinked blend films retain the cholesteric liquid crystalline order (right handed).

Solubility of the Crosslinked Blend Films

Figure 5 shows the dependence of the solubility on the blend composition. The solubility exhibited a maximum around 60/40 and a minimum around 30/70. As described earlier, the pure chitosan film (0/100) cast from the system containing hydrochloric acid dissolved. When the solubility was greater than 70%, the cast film no longer could maintain its form and was finely dispersed in the solution. Interestingly, the film with composition of 30/70 maintained the film form. When glyoxal was used for the crosslinking of the blend, the concentration of hydrochloric acid had to be controlled according to the blend composition. This was because HPC needs hydrochloric acid and no acetic acid, whereas chitosan needs acetic acid and no hydrochloric acid. A comparison between the results for the glyoxal sys-

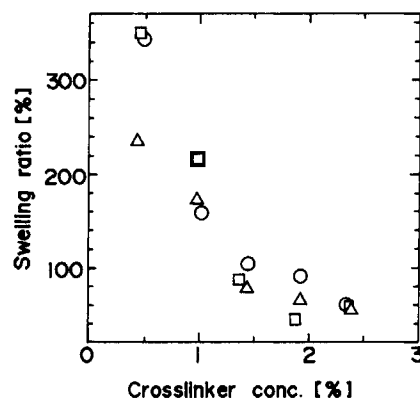


Figure 4 The dependence of swelling ratio for crosslinked blend film (50/50) on glutaraldehyde concentration. Hydrochloric acid and acetic acid concentrations were the same as in Figure 2.

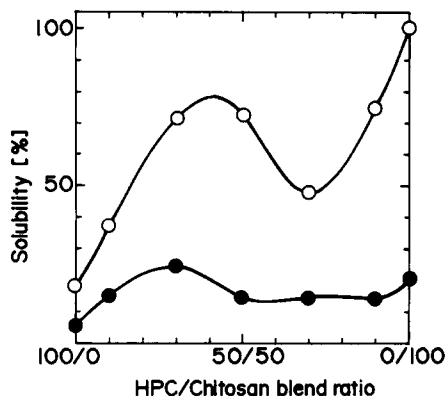


Figure 5 The dependence of solubility for crosslinked blend films on blend composition. Crosslinker: ○ glyoxal, ● glutaraldehyde. Acetic acid concentration: 5.0%. Hydrochloric acid concentration: 1.0%.

tem and those for the glutaraldehyde one showed that the solubility of the film cast from the glyoxal system is greater than that from the glutaraldehyde one. This suggests that the density of crosslinking for the film crosslinked with glutaraldehyde is

greater than that for the film with glyoxal. The swelling behavior of the crosslinked films, as noted earlier, supported this suggestion.

Tensile Properties of the Crosslinked Blend Films

Figure 6 shows the Young's modulus, tensile strength, and elongation at break of the films crosslinked with glyoxal as a function of blend composition. The tensile properties of the pure HPC films (100/0) crosslinked with glyoxal could not be measured because the thin films were too brittle. This was due to the cracks on the edges of the test specimen, which were formed at cutting the specimen from cast films. This was valid for the blend films crosslinked with glutaraldehyde; we had no tensile data in spite of attempting to cut the specimens of films crosslinked with glutaraldehyde. Consequently, we could not grasp the total behavior of our blend system. However, our data shown in Figure 6 strongly suggest that Young's modulus and tensile strength exhibit a maximum and a minimum around 50/50 and 70/30, respectively. This behavior is very

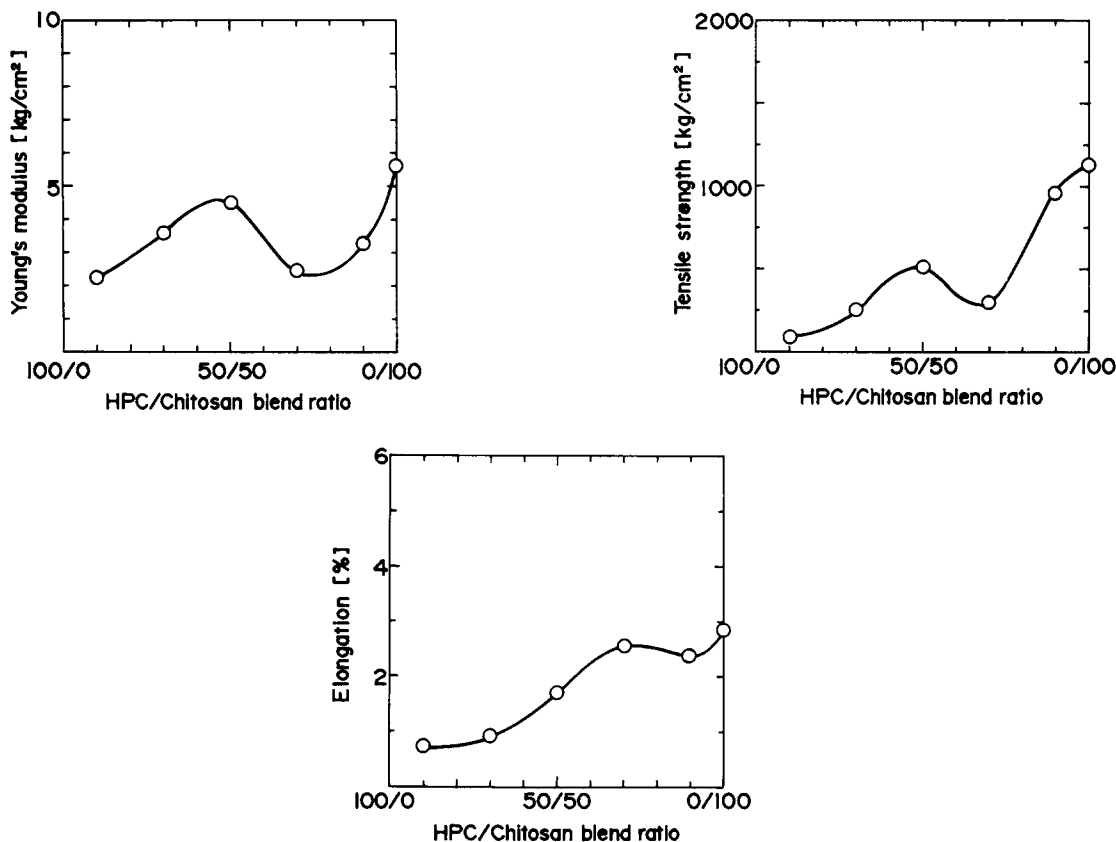


Figure 6 The dependence of tensile properties for crosslinked blend film cast from glyoxal system on blend composition. (a) Young's modulus, (b) tensile strength, and (c) elongation at break.

similar to that of solubility shown in Figure 5. This suggests that the solubility and tensile mechanical behavior of the crosslinked blend films are governed mainly by the morphology of the blend films (i.e., the density of crosslinking). Although Young's modulus and tensile strength tended to increase with an increase in chitosan composition, the elongation did not decrease but tended to increase.

CONCLUSIONS

The blend of HPC and chitosan could be chemically crosslinked by casting the aqueous acetic acid solution of the blend with glyoxal or glutaraldehyde as crosslinker and hydrochloric acid as catalyzer. The crosslinked blend films were amorphous, although the un-crosslinked blend films retained cholesteric liquid crystalline order. The solubility and tensile properties (Young's modulus and tensile strength) of the crosslinked blend films appeared to depend on the blend composition; those properties exhibited a maximum and a minimum around the same blend compositions. The elongation tended to increase with the increase in chitosan composition. The solubility for the crosslinked films cast from the glyoxal system was greater than that from the glutaraldehyde system. This suggests that the density of crosslinking for the film cast from the glutaraldehyde system is greater than that from the glyoxal system.

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