

Preparation and Properties of Hydrogels Based on Hemicellulose

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ABSTRACT: Xylan with glucuronic acid functionalities, separated from birchwood, was converted into hydrogels by dissolving it together with chitosan in acidic conditions. The hydrogels were formed at certain xylan/chitosan compositions. The mechanism of the gel formation was investigated with FTIR. Complexation between glucuronic acid functionalities of xylan and amino groups of chitosan is suggested to be responsible for network formation. The swelling behavior of these hydrogels was studied at various pH levels and salt concentrations, and the hydrogels responded in a reversible manner to various stimuli. DMA of the films showed separated transitions that may correspond to different phases. Imaging with AFM in TappingMode™ of the surfaces indicated discrete xylan and chitosan phases. A sponge-like microporous structure, as shown with SEM, was formed when a hydrogel was freeze dried. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1661–1667, 1998

Key words: xylan; chitosan; hydrogel formation; swelling

INTRODUCTION

Among plant polymers, cellulose has been utilized as a useful material since the beginning of civilization. However, two other important plant polymer groups, namely hemicelluloses and lignin, have not yet found broad industrial applications. Recent studies carried out by a number of research groups have pointed out some new applications for lignin polymers. Adhesives, coatings, and foam products have been prepared by the conversion of isolated lignin into thermosetting resin products. Other examples are surface active agents, engineering plastics, and admixtures for concrete and cement.^{1–6} Hemicelluloses, even though they are as abundant as cellulose in many plants, have not been commercially utilized more

than as a sizing agent in paper to some extent and as a source of xylitol.⁷ However, recent research has begun to find new applications for hemicelluloses. Examples of future applications of hemicelluloses are as food additives, thickeners, emulsifiers, gelling agents, adhesives, and adsorbents.⁸ Hemicelluloses have also been proved to be a good binder for charcoal/coal briquettes.⁶ Several interesting discoveries have also recently been made in the biomedical field. For example, hemicelluloses have been shown to work as anti-tumor agents.⁸

The amount of hemicellulose in wood can be quite substantial. In hardwood such as birch or aspen, up to 30% of the mass may consist of hemicellulose. In plants, hemicellulose is synthesized by a different path from that of cellulose and, in contrast with cellulose, many hemicelluloses are branched, are composed of a mixture of different sugars, and have various substituents. Owing to these factors, they are not crystalline, and many of them are water soluble. Hemicelluloses have a

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relatively low degree of polymerization (typically less than 200). The most commonly existing sugars that build up polysaccharides are D-glucose, D-mannose, D-xylose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid.⁹ Hemicelluloses have been reported already in the 1950s to be associated with lignin (LCC)¹⁰ with bonds later proved by other authors^{11,12} to be covalent and, furthermore, hydrogen bonded to cellulose.⁹ During pulping processes, the purpose of which is to separate cellulose fibers from solid wood, hemicelluloses are completely or partially degraded together with the lignin matrix, depending on the pulping process used. This is the chief reason why the material properties of the polymeric hemicelluloses have not yet been recognized. Recent studies demonstrated that xylan-rich noncellulosic carbohydrate polymers can be isolated from agricultural residues using an alkali extraction process combined with ultrafiltration.¹³

There is an increased interest in preparing new materials for a rapidly growing list of biomedical applications. Since the introduction of hydrogels based on synthetic polymers such as HEMA by Wichterle and Lim,¹⁴ studies of interpenetrating polymer networks and ionic complex networks based on natural polymers have attracted the interest of several scientists.¹⁵⁻¹⁸ In the present study, xylan with glucuronic acid functionalities separated from birchwood was converted into hydrogel by dissolving it together with chitosan in acidic conditions. Both the mechanism of gel formation and the swelling properties were investigated.

EXPERIMENTAL

Materials

Xylan, separated from birchwood, purchased from Sigma, Germany (product No. X-0502), and chitosan, ProFloc 340, ProNova Biopolymers, Norway, with a degree of deacetylation of 77% were used without further purification. The sugar content of the xylan was determined by STORA Corporate Research, Sweden, using gas chromatography determination after hydrolysis and silylation and is summarized in Table I. This analysis does not give the percentage of acidic sugars. It also degrades the linkages between xylose and uronic acid, which causes a certain loss of xylose. The

Table I Sugar Analysis of Hemicellulose From Birchwood

Sugar	Content (%)
Galactose	0.1
Glucose	0.3
Mannose	0.0
Arabinose	0.2
Xylose	73.2
Uronic acid	—
Hydrolysis residue	0.9
Total	74.6

amount of carboxyl groups was 0.34 mmol/g xylan, as found by potentiometric titration.

Preparation of Films

Solutions were made from xylan with various amounts of chitosan by mixing in dry form and stirring into acidified water. This was followed by heating to 95° C, at which it was maintained for 20 min. Hydrochloric acid was used in amounts equal to the amount of amino groups in the chitosan plus 0.9 mmol per grams polysaccharide in total. The solutions were cooled to room temperature and poured onto polystyrene dishes. The solutions were then dried into films of constant weight under ambient conditions. The thickness of the achieved films was typically 50 μ m.

Water Uptake

Small pieces (ca. 1.5 \times 1.5 cm) of films were placed in a glass dish of known weight. Deionized water (25 mL) was added, left for 30 min, and then carefully removed, leaving the sample on the dish. The dish was dried with a Kleenex and weighed. The swelling ratio (S) was defined as: (weight of hydrated gel – weight of dry gel)/(weight of dry gel). Water uptake was also measured as a function of different pH level and salt concentrations. The results were plotted as mean averages of at least five samples with 95% confidence intervals.

FTIR

FTIR spectra were recorded using a Perkin-Elmer System2000 FTIR instrument with a chamber for purging with dried air. The ATR technique was employed, and samples were dried in vacuum for

12 h at 50°C before analysis. Spectra were recorded at 4000–400 cm⁻¹.

Dynamic Mechanical Analysis

DMA of chitosan films and xylan/chitosan films of various compositions were carried out using a Rheometric Solid Analyzer (RSA 2). Samples were tested in uniaxial tension mode at a heating rate of 5°C/min and a frequency of 1 Hz. The glass transition temperature was defined as the temperature corresponding to the maximum in the tan δ curve.

Atomic Force Microscopy

The surfaces of the films were investigated with a Digital Instruments NanoScope III Atomic Force Microscope in TappingMode.TM The AFM was fitted with a NanoScope III Controller with a Phase Extender Box. A Dimension 3000 Large Sample AFM with type G scanner and standard silicone tip were used.

Freeze Drying and SEM

A film of 80% xylan and 20% chitosan was placed in water in a round-bottomed flask. After 1 min of soaking, the excess water was removed with a pipette. The flask was immersed in liquid nitrogen for 2 min and adapted to a vacuum pump for sublimation overnight. The structure was examined with Zeiss DSM 940A SEM.

RESULTS AND DISCUSSION

Preparation of the Films

Solutions of pure xylan, pure chitosan, and various mixtures of the two were cast onto polystyrene plates. They were dried under ambient conditions to constant weight, and the film formation was evaluated. Pure xylan solution did not form films, but the addition of as little as 5% chitosan resulted in the formation of flakes. At 10% chitosan and above, continuous, self-supporting films were achieved.

Swelling Properties

All films were investigated with regard to water solubility and water uptake. As mentioned above,

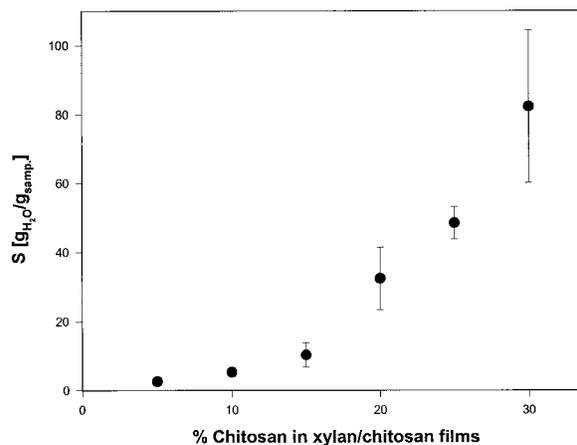


Figure 1. The effect of xylan/chitosan concentration on swelling properties.

pure xylan did not form films, but the fragments achieved did not appear to absorb significant amounts of water. As the films were prepared with chitosan in increasing concentrations, they absorbed water. Films with a chitosan content below 30% swelled in water and formed hydrogels. Figure 1 shows the effect of chitosan content on the swelling ratio (S), as defined in the experimental section. The swelling ratio was recorded after 30 min exposure to water, which was found to be sufficient to reach equilibrium swelling. The degree of swelling strongly depended on the chitosan content. The presence of up to 15% chitosan does not greatly affect the degree of swelling. The addition of 15 to 30% chitosan results in a considerable increase in water uptake. It should be noted that, at 30% chitosan, a large scattering of the swelling measurements was obtained. Above 30% chitosan, the samples started gradually to dissolve during swelling measurements. Pure chitosan films were readily dissolved in water. The large scattering when measuring swelling of 30% chitosan films is probably a result of partial dissolving.

The hydrogels were also exposed to variations in external stimuli, such as pH and salt concentration. Figure 2 shows the effect of cyclic swelling in water and 0.1M sodium hydroxide solution of a 75% xylan/25% chitosan hydrogel. It is seen that the hydrogel responds in a reversible manner to changes in environmental stimuli. The hydrogel swells significantly less when the swelling media is NaOH. Figure 3 illustrates the swelling of films with 80% xylan and 20% chitosan in buffer solutions ranging from pH 2 to 12. The ionic strength (I) was adjusted to 0.075M and 0.15M

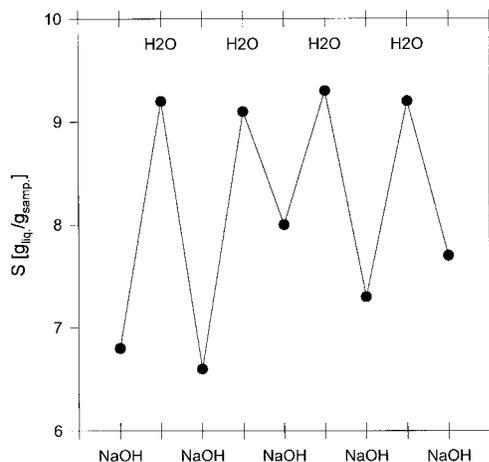


Figure 2. The effect of cyclic swelling in water and 0.1M sodium hydroxide solution on swelling behavior of a hydrogel.

with NaCl. The swelling is proposed to be caused by the difference between the osmotic pressure of mobile ions in the gel and in the surrounding solution, described by the Donnan theory.^{19,20} The gel contains ionizable groups fixed to the network polymers, carboxyl groups that form carboxylate ions at the high pH range, and amino groups that form ammonium ions at the low pH range. These ions are confined within the gel. Smaller ions and water have free passage between the gel and the solution, and chemical equilibrium exists in and between the two phases. The gel will have an excess of mobile ions, and an osmotic pressure expands the gel until limited by the cohesive forces of the network. As seen in the figure, the degree of swelling is higher at both low and high pH than it is at neutral pH. At very high pH, the swelling is rapidly reduced. This is explained by the acidic groups being completely dissociated and that a further increase in the amount of mobile ions leads only to a decrease in osmotic pressure. The effect of the addition of NaCl can be explained on the same basis. Increasing the total amount of ions decreases the ratio of ions between the interior of the gel and the surrounding solution. At neutral pH, the degree of swelling (S) was slightly below 4 for both $I = 0.075 M$ and $I = 0.15 M$. Swelling of a film of 80% xylan and 20% chitosan in deionized water resulted in a degree of swelling of slightly below 40, as shown in Figure 1.

Mechanism of Hydrogel Formation

The mechanism of the hydrogel formation was investigated with FTIR using a model system. In

these experiments, chitosan was dissolved and mixed together with glucuronic acid, as we suspect that complexation between glucuronic acid functionalities of birch xylan and amino groups of chitosan is responsible for the hydrogel formation. Experiments have been performed by other authors that indicate that complexation between the amino groups in chitosan and carboxyl groups in xanthan is responsible for gel formation.¹⁷ Their experiments showed that a strong band appeared in the FTIR spectra at 1620 cm^{-1} as a result of the complexation, and that complexation was more pronounced at higher pH.

Figure 4 shows a region of $1900\text{--}1450 \text{ cm}^{-1}$ of spectra of films of chitosan with glucuronic acid in an amount equal to the free amino groups of the chitosan. The films were prepared at different pH levels ranging from 1.6 to 4.1. The spectra were normalized against the band height at 1060 cm^{-1} corresponding to the saccharide internal ether stretchings.²¹ At the higher pH, it is seen that the peak at 1726 cm^{-1} declines and a strong band arises at $1615\text{--}1605 \text{ cm}^{-1}$, probably due to deprotonation of the carboxylic groups in glucuronic acid and complexation with chitosan.

Morphology

Dynamic mechanical measurements were carried out on a film composed of 65% xylan and 35% chitosan and on a pure chitosan film. Figure 5 shows the spectra. Pure chitosan film shows one maximum in $\tan \delta$ at 204°C . Films composed of 65% xylan and 35% chitosan show one large $\tan \delta$

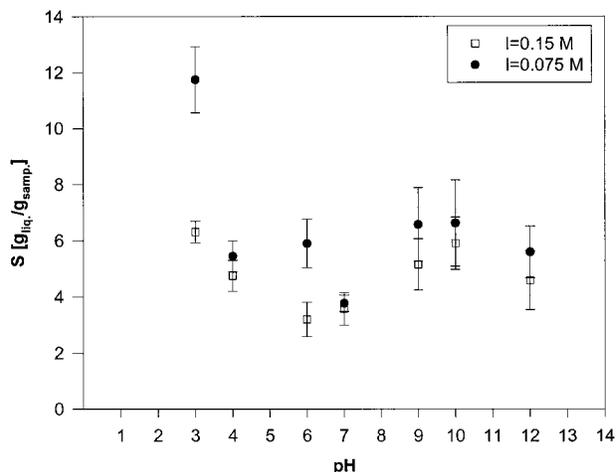


Figure 3. Swelling behavior of films at different pH and ionic strength.

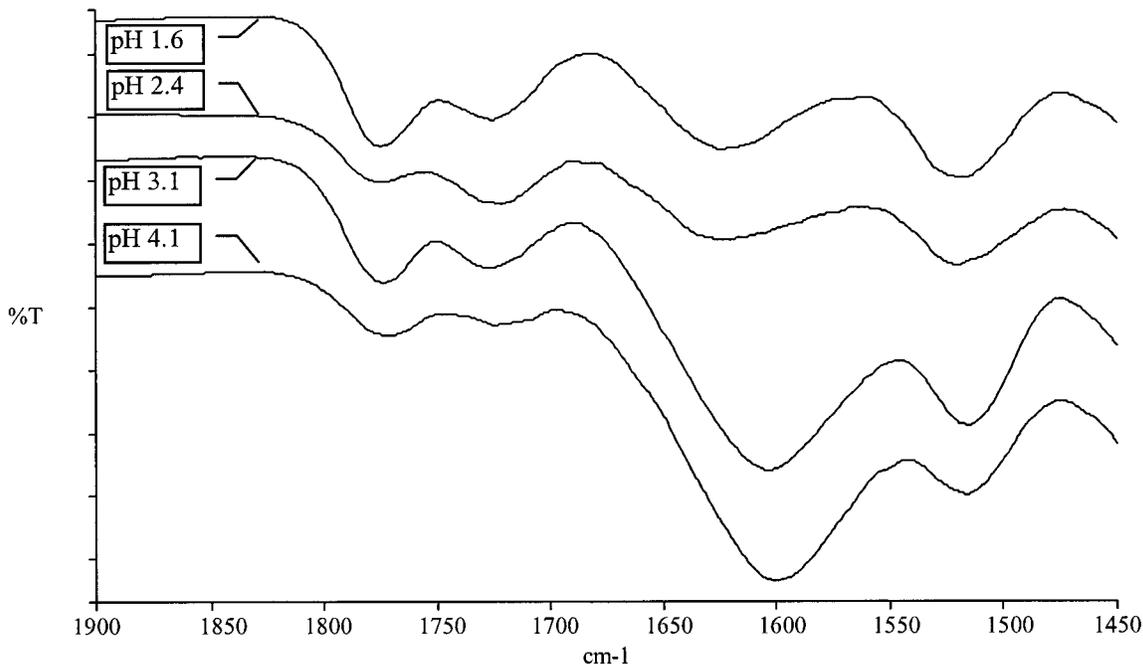


Figure 4. FTIR spectrum of films of chitosan and glucuronic acid prepared at various pH levels.

peak at 180°C and a smaller one at 204°C. The transition at 180°C is not observed in the pure chitosan film, and it corresponds well to the expected glass transition temperature of xylan.^{22,23} This indicates that xylan and chitosan may be present in two different phases. As the DMA measurements indicated the presence of two phases, the surfaces of the films were investigated using AFM in TappingMode™. AFM has recently been successfully used for imaging polysaccharide gels

and surfaces of amorphous films.^{24,25} First, the surfaces of xylan flakes (xylan did not form film) were investigated, the results of which are shown in Figure 6. The surface is composed of small particles that are loosely connected with each other. When chitosan is added, interactions between chitosan ions and glucuronic acid promote some mixing, and result in film formation. At 10% chitosan, an almost homogenous film is formed. When the concentration of chitosan is increased and reaches

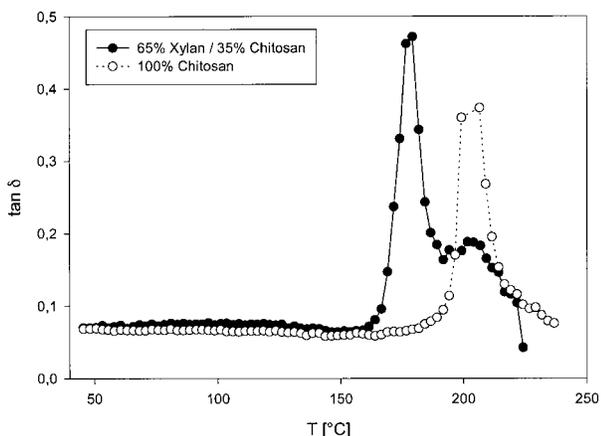


Figure 5. DMA spectra of film of 65% xylan and 35% chitosan and film of chitosan.

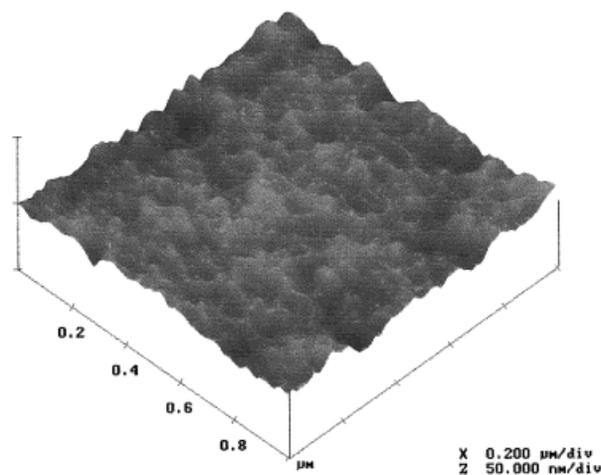


Figure 6. AFM image of xylan film.

30%, interesting features emerge. Figure 7 shows the image of the film composed of 70% xylan and 30% chitosan. It is seen that the picture illustrates fibril-like features. Thus, fibril-like features appearing in the image may well correspond to the chitosan phase. These results would agree with DMA studies indicating the presence of two different phases.

Formation of Microporous Structures

The physical form of the hydrogel has a major effect on the efficiency of the liquid absorption process. For example, the swelling of the film is affected by the kinetics of the diffusion process. Microporous materials with a well-defined pore structure and hydrophilic surface are of interest because of their attractive liquid transport properties. When water-swollen hydrogel prepared from 80% xylan and 20% chitosan was freeze dried, an opaque film was achieved. The structure formed by this process was investigated with SEM. Figure 8 shows a cross-section of the material prepared in such a way. It has a sponge-like microporous structure with relatively well-defined pores in the range of 5–10 μm . The effect of processing conditions upon the porosity of the structures and the effect of the structure upon absorption properties will be investigated in our laboratories in the nearest future.

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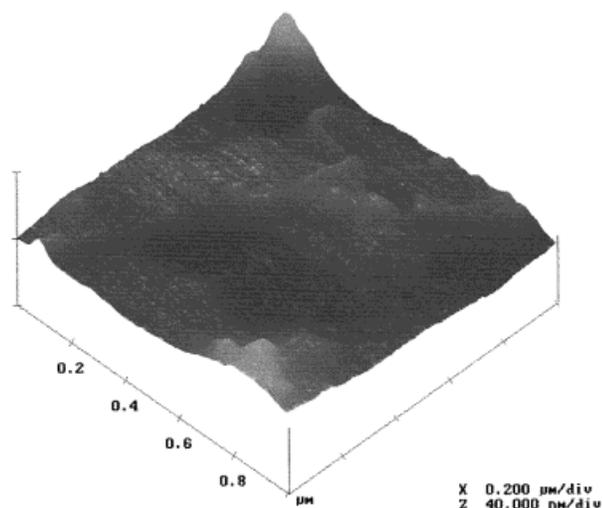


Figure 7. AFM image of film of 70% xylan and 30% chitosan.

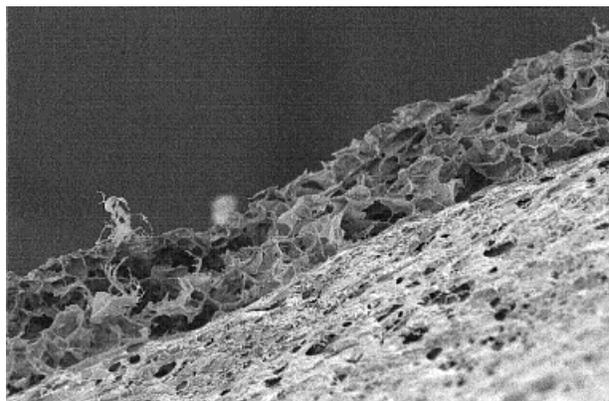


Figure 8. SEM picture of cross-section of structure formed upon freeze drying of a film of 80% xylan and 20% chitosan.

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