

Comparison of water retention and thermal properties of various polysaccharides, their derivatives and blends

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The Philippines has an abundance of polysaccharide resources such as different forms of cellulose (*nata de coco*, kapok, ramie, banana fiber, etc.). This paper presents some polysaccharides hydrogels, which have numerous higher value applications. Hydrogel properties are related to water retention property, which in turn can be associated with thermo- or pH-sensitivity. These properties can be modified through derivatization. Acetylation significantly decreases the solubility of the polysaccharide in water and its ability to form hydrogels. The carboxymethyl group decreases water retention without losing its hydrophilicity altogether. Semi-interpenetrating networks, on the other hand, can have controlled properties depending on the amount of crosslinking. These are observed with the help of thermal analysis and equilibration experiments.

Keywords: dextran; κ -carrageenan; *nata de coco*; chitosan; poly-(N-isopropylacrylamide); carboxymethyl dextran; dextran sulfate; dextran triacetate; cellulose triacetate; semi-interpenetrating network

INTRODUCTION

Current efforts to study and modify polysaccharides indicate significant interest in their potential applications, particularly those involving properties like biocompatibility, mechanical strength, biological activity and water retention. The Philippines is abundant in these resources but still needs to utilize them for higher value products.

Polysaccharides and other hydrophilic polymers form hydrogels, which have numerous applications such as in controlled drug release, chemomechanical actuators, immobilized enzyme reactors, solute recovery reagents, and environment-sensitive membranes [1]. The degree to which they swell is related to their water retention property. Water retention can also be related to thermal properties, especially if critical solution temperatures can be observed.

This paper focuses on the water retention and thermal properties of bacterial cellulose (*nata de coco*), dextran, chitosan, κ -carrageenan, their derivatives and blends. Figure 1a b give the structures of these polysaccharides and their derivatives.

EXPERIMENTAL

Preparation of polysaccharide derivatives

Dextran synthesized from a locally isolated strain of *Leuconostoc mesenteroid* was provided by the Philippine Dextran Development Foundation Inc. *Nata de coco* slabs were cut into 1-inch cubes, pressed, and air-dried for five days. Chitosan was purchased from Fluka with medium molecular weight. κ -Carrageenan was provided by Shemberg and the Marine Science Institute (UP Diliman). All other reagents used were analytical grade.

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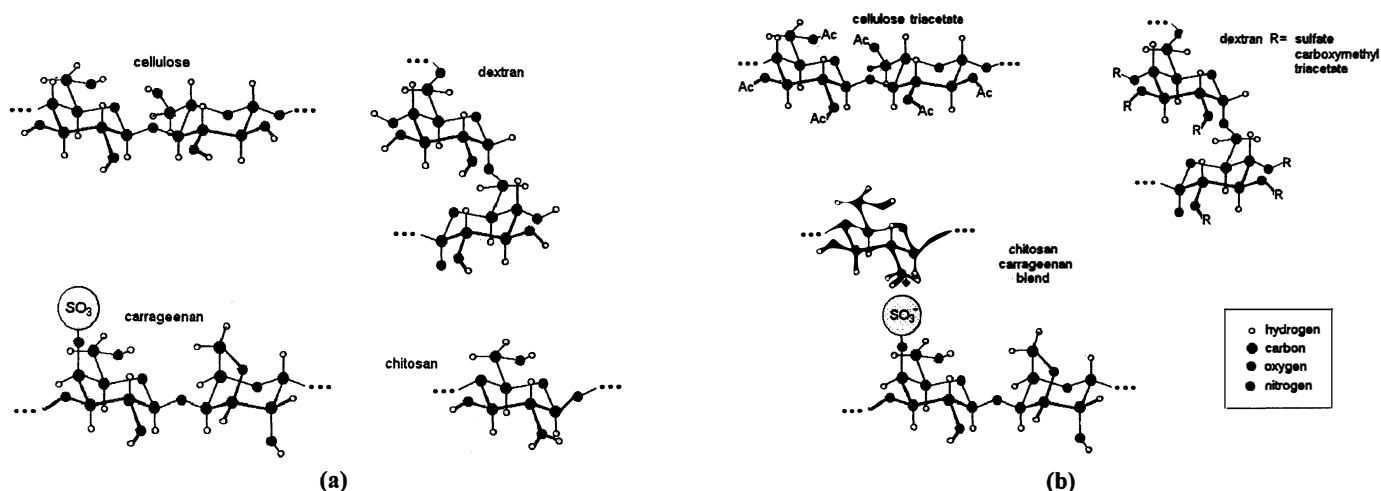


Fig. 1. (a) Polysaccharides used in this study; (b) Polysaccharide derivatives.

Carboxymethyl dextran (CMD) [2]. Dextran was dissolved in chloroacetic acid solution containing NaOH, heated between 60–90°C for 3 h, then mixed with ethanol. The sodium salt of CMD was washed with distilled water then acidified to pH 5 with acetic acid. Free CMD was precipitated with ethanol, oven-dried at 50°C for three days.

Dextran sulfate (DS) [2]. A slurry of dextran in formamide was heated for 30 min at 60°C, then cooled to room temperature. Chlorosulfonic acid was stirred into the mixture. The DS was isolated by pouring into acetone. The precipitate was washed with acetone and ethanol, and then converted to the sodium salt with NaOH. The salt was precipitated with ethanol, washed and oven-dried at 50°C for three days.

Dextran triacetate (DTA) [2]. Dextran was pre-treated with glacial acetic acid for three days. This was mixed with toluene, acetic acid and a catalytic amount of 60% HClO₄. The mixture was stirred for 70 h at 15–32°C. The product was centrifuged, washed repeatedly with ethanol, and air-dried.

Cellulose triacetate (CTA) [3, 4]. The *nata de coco* samples were pre-treated with glacial acetic acid. This was mixed with toluene, acetic acid and a catalytic amount of 60% HClO₄. The mixture was stirred for 60 h at 15–32°C or reacted in an ultrasonic bath (L&R Solid State/Ultrasonic T-14B) for an hour. The mixture was decanted, washed repeatedly with ethanol, and air-dried.

κ-Carrageenan/chitosan (CChi). Aqueous solutions of κ-carrageenan and chitosan were mixed. Glutaraldehyde, a cross-linking agent for chitosan, was added to the mixture in mol ratios of 1%, 3%, and 5%. All the samples were heated in boiling

water bath for 30 min, centrifuged, then decanted. The samples were washed with distilled H₂O several times then with acetone. They were vacuum-dried for two days.

κ-Carrageenan with/(x)poly-(N-isopropylacrylamide) semi-interpenetrating network (CPx). A 1M solution of N-isopropylacrylamide (Sigma) in deionized water and methanol (50/50) was prepared in the presence of 0, 1, 3, and 5 mol% of the cross-linking agent ethyleneglycol dimethacrylate (EGDMA). Ten mL of 1% κ-carrageenan in deionized water was added for every 10 mL 1M N-Isopropylacrylamide. The mixture was stirred and nitrogen was bubbled through the solution for 20 min. After the addition of 1% (w/w) 2,2'-azobisisobutyronitrile (AIBN, Chem Service) as initiator, the reaction mixture polymerized in a vacuum-oven at 60°C and, 15 mm Hg for 3 h. After optimizing the effect of cross-linker, CPx₁ (1 mol% cross-linker) was used with varying proportions of carrageenan relative to poly-(N-isopropylacrylamide) (pIPAAm) (i.e., 1.3, 2.7, and 3.9 mol%).

Chitosan with/(x)poly-(N-isopropylacrylamide) semi-interpenetrating network (ChiPx) [5]. A 1M solution of N-Isopropylacrylamide (Sigma) in deionized water was prepared in the presence of 1 mol% of the cross-linking agent ethyleneglycol dimethacrylate (EGDMA). Chitosan solution was added to 1M N-isopropylacrylamide to make 2.8, 5.6, and 8.5 mol% chitosan relative to pIPAAm. To this was added 5% HCl. The mixture was stirred and sonicated for 10 min. After the addition of 1 wt.% 2,2'-azobisisobutyronitrile (AIBN, Chem Service) as initiator, the reaction mixture polymerized in a vacuum-oven at 60°C, 15 Hg, for 24 h.

Water retention and swelling properties

pH-sensitivity. The chitosan-pIPAAm (ChiPx₁) semi-IPN hydrogel was allowed to swell in 10 mL deionized water at different pH values (1.45, 3.88, 7.03, 9.00 and 12.5) for 3 h, after which the gels were removed from the swelling medium. Excess water was blotted out and the % water retention was calculated according to the following expression:

$$\% \text{ water retention} = (W_s - W_d) / W_s \times 100$$

where W_s was the weight of the swollen hydrogel and W_d was the weight of the dry hydrogel.

Thermo-sensitivity. The carrageenan-pIPAAm (CPx₁) semi-IPN hydrogel was allowed to swell in 10 mL deionized water at different temperatures, after which the gels were removed from the swelling medium. Excess water was blotted out and the % water retention was calculated accordingly.

RESULTS AND DISCUSSION

Dextran and its sulfate derivative were the only polysaccharides which were readily dissolved in water. DTA, on the other hand, was not water-soluble. Among the polysaccharides that formed hydrogels, CMD had the highest water retention while CTA had the lowest water retention (Table 1). CTA and carrageenan-pIPAAm semi-IPN with 1 mol% cross-link (CPx₁) exhibited the greatest dependence on pH.

Acetylated derivatives. Acetylation reduced the hydrophilicity of the material as the water retention behavior observed with *nata de coco* and dextran. DTA remained suspended in water. CTA may not be completely triacetylated [6], giving it some swelling ability. Interestingly, the pH-dependence of swelling of CTA was more pronounced than for cellulose. This may indicate a degree of hydrolysis occurring in the different media.

Table 1. Water retention of various polysaccharides and their derivatives (% by weight)

	pH = 2	pH = 4	pH = 5	pH = 7	pH = 9
Chitosan	–	–	–	88.42	83.43
CChiX ₀	–	92.84	–	93.58	93.64
CChiX ₅	–	91.05	–	91.36	91.75
CMD	94.1	–	95.2	95.6	dissolved
Cellulose	85.7	–	85.7	91.3	85.7
CTA	50	–	40	65.5	60
PIPAAm	–	–	–	76.17	–
CPX ₁	–	85.17	–	79.52	95.88
CPX ₃	–	83.55	–	71.39	85.17
CPX ₅	–	87.54	–	86.67	85.18
CPX	–	84.35	–	83.1	88.48

Carboxymethylated dextran (CMD). The carboxymethyl group (–CH₂COOH) is more hydrophobic compared to hydroxy and sulfate groups, but could still be involved in H-bonding with the solvent. Thus, CMD formed a hydrogel, with high swelling power when immersed in different solutions (Table 1).

κ-Carrageenan/chitosan (CChi). Electrostatic interaction of NH₂-containing chitosan with sulfate-containing κ-carrageenan led to a blend that gave higher water retention (Table 1) relative to chitosan alone. On the average, the presence of cross-linker decreased the swelling capacity, though not significantly. The presence of κ-carrageenan decreased the pH-sensitivity of chitosan. It is possible that the amino group of chitosan prioritized the interaction with sulfate group of κ-carrageenan, rendering its active site less available for solvation.

κ-Carrageenan-pIPAAm semi-IPN (CPx₁). The temperature sensitivity is significant for this system. The hydrogels collapsed between 25–32°C. A decrease in temperature sensitivity was

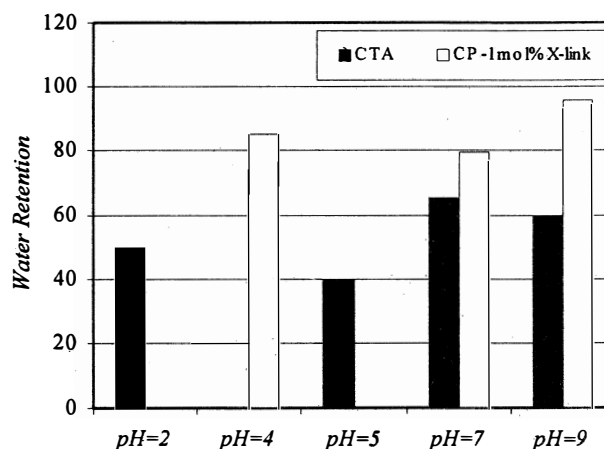


Fig. 2. Water retention of CTA and carrageenan-pIPAAm Semi-IPN (CP-1mol% X-link) at various pH.

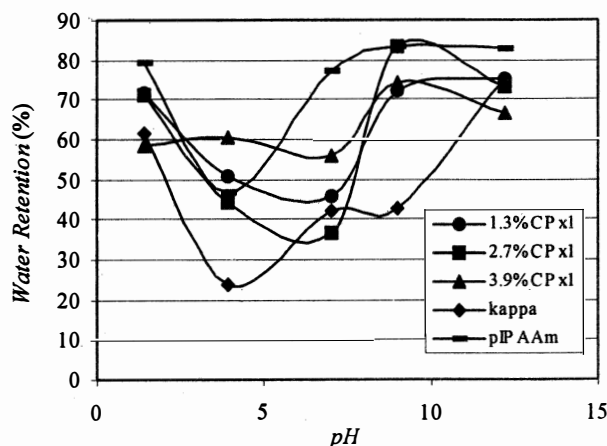


Fig. 3. Swelling capacity of CPx₁ hydrogel at different pH.

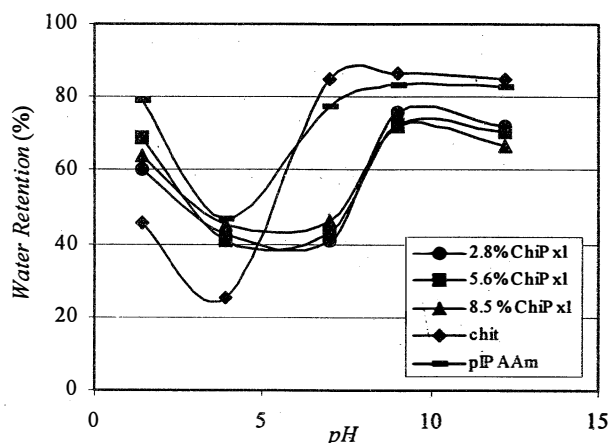


Fig. 4. Swelling capacity of ChiPxl hydrogel at different pH.

Table 2. Major degradation of various polysaccharides from TGA (°C).

Sample	Onset Temperature	Midpoint
Dextran	312	353
CMD	289	333
DS	228	258
DTA	287	370
Cellulose	341	361
CTA	358	373
Chitosan	307	333
Carrageenan	212	235
CC	220	259
CC-1% X-link	230	262
CP	397	422
CP-1% X-link	397	419
CP-3% X-link	410	434
CP-5% X-link	402	427

observed as the amount of cross-linker increased. Rigidity of the polymer limited the conformational change from hydrophilic to hydrophobic structure that probably caused the decline in temperature sensitivity. However, the presence of κ -carrageenan allowed a significant amount of water to be retained in the network. In terms of pH, pure carrageenan and pIPAAm collapsed at pH 3.9, while the blends collapsed at pH 7 (Fig. 3).

Chitosan-pIPAAm semi-IPN (ChiPx). In Fig. 4, the blends retained its collapsed state from pH 7 to 3.9, which means that the material is stable at that pH range and that no other effects could be induced.

Thermal properties. Derivatization of polysaccharides led to a different degradation pattern confirming the chemical changes in their structures. Cellulose and CTA had the highest thermal resistance at 341°C and 358°C, respectively, and DS the lowest at 228°C (Table 2).

CONCLUSION

Modification of polysaccharides through derivatization and blends is a way of changing their water retention properties.

Acetylation significantly decreases solubility of dextran in water. On the other hand, acetylation decreases the water retention of cellulose up to 56% of the original value. CMD has the highest water retention of the polysaccharide derivatives while CTA has the lowest water retention (down to 40%, at pH5).

The presence of carrageenan in the blend with chitosan and in the semi-IPN of pIPAAm increases water retention of these polymers. Another way of looking at this is that chitosan and pIPAAm decreases the water retention of carrageenan. Both ways, modified properties are observed.

The pH sensitivity depends on the functionality of the polymer, which also affects its swelling property. CTA and the carrageenan-pIPAAm semi-IPN with 1 mol% cross-link exhibits the greatest dependence on pH.

Cellulose and its triacetate derivative have the highest thermal resistance at 341°C and 358°C, respectively, and DS the lowest at 228°C.

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