Effect of Addition of Saccharides on Gelation of Aqueous Poly(vinyl alcohol) Solutions

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Received 19 January 1999; accepted 23 March 1999

ABSTRACT: The properties of poly(vinyl alcohol) (PVA) hydrogels containing saccharides (D-xylose, D-fructose, D-glucose, and maltose) were examined. The effect of the addition of saccharides to PVA hydrogels on their melting temperatures was remarkable when the gels were chilled at 0°C with saccharide contents above 40 g/dL. Particularly, the melting temperature was the highest for PVA hydrogels with glucose and above 73°C at the polymer concentrations above 6 g/dL. Namely, the enthalpy of the thermal dissociation of the junctions of the spatial network ΔH was the highest of the four saccharides (glucose > fructose > maltose > xylose) and 150 kJ/mol for the hydrogels with the glucose content of 60 g/dL. The uniform preservation of saccharides and water in their gels were the highest for the gels with fructose during standing for a long time in air after freeze-drying. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1298–1303, 1999

Key words: poly(vinyl alcohol); saccharides; mixed solution; gelation; dynamic modulus; syneresis

INTRODUCTION

The thermal and mechanical stabilities of poly(vinyl alcohol) (PVA) hydrogels have been achieved by repeating the freezing/thawing cycle,[1,2] using the mixed solvents of water/organic liquid,[3–9] and using the syndiotacticity-rich PVA,[10,11] etc. Moreover, the hydrogels obtained from the aqueous PVA solutions with saccharose were also ascertained to be thermally and mechanically stable.[12]

The PVA hydrogels released almost all water molecules after standing for a long time in air and did not maintain raw form.[12] However, if saccharose was added into PVA hydrogels, the vaporization of water molecules from the hydrogels was considerably restrained.[12]

The present study examined the effects of the addition of some saccharides on the melting temperature of PVA hydrogels and the volume change of PVA hydrogels with standing in air. Moreover, the properties of the PVA hydrogels with some saccharides were examined.

EXPERIMENTAL

Samples

An atactic PVA (*a*-PVA) offered from Unichika Chemical Co. Ltd. were used, which had the degree of polymerization of 1300, the syndiotactic dyad content of 49.1%, and the degree of saponification of 99.9 mol %. Distilled water was used as a solvent. Saccharides are D-xylose, D-fructose, D-glucose, saccharose, and maltose, which were all special grade (Wako Pure Chemical Industrial, Ltd., Japan).

The aqueous saccharide solutions with the concentration of 0–50 g/dL for xylose and maltose,

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Contract grant sponsor: Ministry of Education, Science, Sports and Culture of Japan; contract grant number: 10CE2003 (Grant-in-Aid for COE Research).

Journal of Applied Polymer Science, Vol. 74, 1298–1303 (1999)
 CCC 0021-8995/99/051298-06

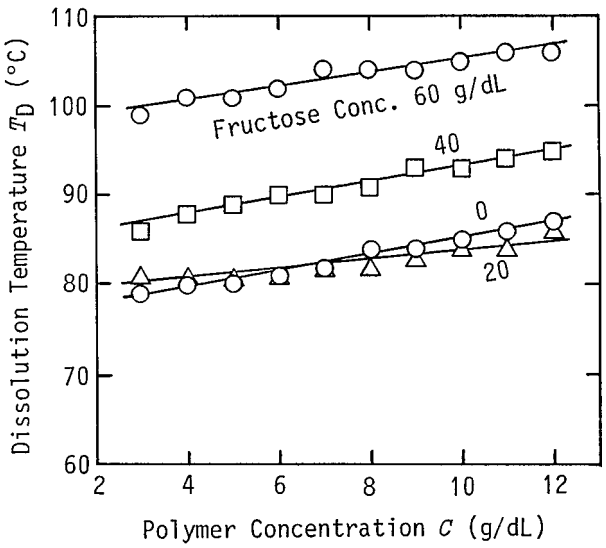

Figure 1 Relations between the dissolution temperature of a-PVA into aqueous fructose solutions and polymer concentration.

and 0–60 g/dL for fructose and glucose were prepared. The a-PVA (polymer concentration: C = 3–12 g/dL) was dissolved in the aqueous solutions containing the saccharides in a well-stirred poly(ethylene glycol) (PEG) bath heated at a rate of 1°C/min. The dissolution temperature (T_D) of a-PVA was examined.

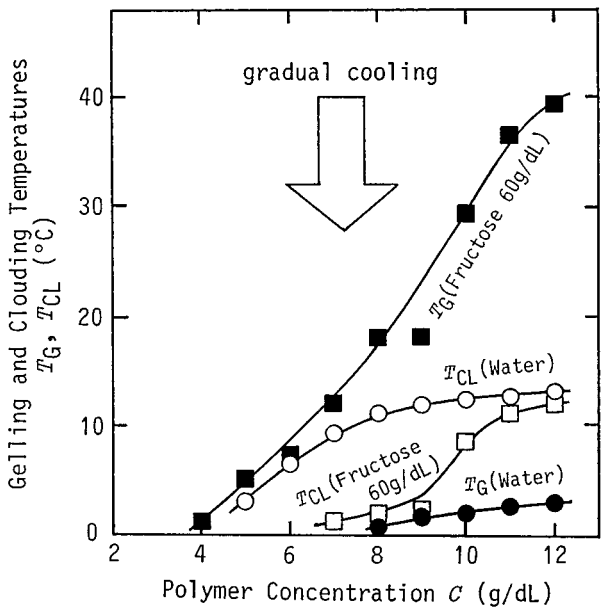

Figure 2 Relations between gelling or clouding temperatures of aqueous a-PVA solutions with or without fructose during gradual cooling and polymer concentration.

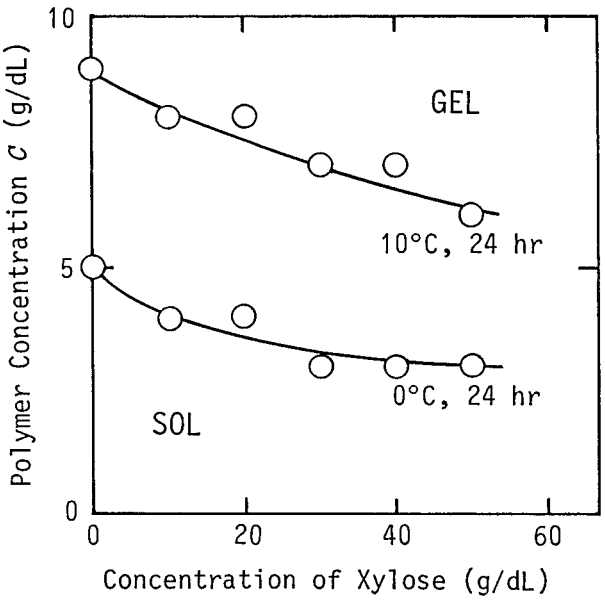

Figure 3 Relations between critical polymer concentration of gelation and xylose content for aqueous a-PVA solutions that stood at 10 or 0°C for 24 h.

The aqueous a-PVA solutions containing saccharides were cooled from 120°C to room temperature in the PEG bath and then to 0°C in a water bath, during which the clouding and gelling temperatures (T_{CL} and T_G) of the solutions were examined.

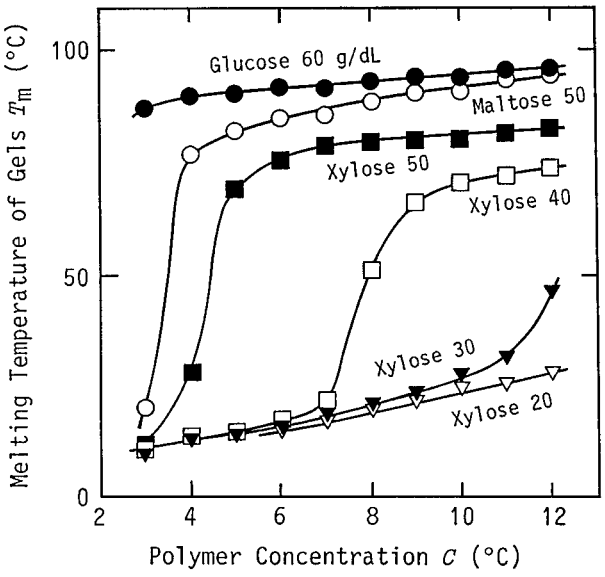

Figure 4 Relations between melting temperatures and polymer concentration for a-PVA hydrogels with saccharides chilled at 0°C for 24 h.

Table I Enthalpy of Thermal Dissociation of Junctions of Spatial Network ΔH for α-PVA Gels with Various Saccharides

Saccharide Content (g/dL)	ΔH (kJ/mol)				
	Xylose	Fructose	Glucose	Saccharose	Maltose
50	64	—	—	100	82
60	—	116	150	130	—

Melting Points of Gels

The α-PVA solutions described above were warmed at 120°C in a well-stirred PEG bath and gelled by chilling at 0−40°C for 24 h. The test tubes with gels were placed upside down in a well-stirred water bath. The bath was warmed from 0 to 25°C at a heating rate of 0.5°C/min. At temperatures above 25°C, the test tubes with gels were placed in a well-stirred PEG bath and warmed at the same rate. The temperature at which a gel flowed and fell to the bottom of the tube after air entered it was regarded as the melting temperature, T_m. The enthalpy of the thermal dissociation of the junctions of the spatial network ΔH was estimated by the Eldridge–Ferry equation.[12]

Solvents Preserved in Gels

15 mL portions of α-PVA (C = 4, 5, 10 g/dL) solutions were poured into plastic photo-film cases (2.9 cm diameter). The concentrations of saccharides were 0, 20, 40, and 50 g/dL for xylose and maltose and 0, 20, 40, and 60 g/dL for fructose and glucose. The cases with solutions were held in a freezer at −32°C for 18 h and thawed at room temperature for 6 h. This freezing/thawing process was called one cycle. After three cycles, the gels obtained were put into a beaker covered by aluminum foil with many pinholes, stood in air at room temperature, and weighed after standing for 24 h. The solution that transuded on the gel surfaces was wiped off by filter paper before weighing. The weight of gels after three cycles of freezing/thawing, W_0, and that of gels after standing in air for t days, W_t, were examined. $(W_t/W_0)_{eq}$ was the weight ratio when W_t arrived to the equilibrium values of syneresis.

Dynamic Modulus

Dynamic compressive modulus was measured using a TMA 4000 apparatus from MAC Science Co., Ltd., Japan. After three cycles of the freezing/thawing process, the Young's modulus of the α-PVA gels obtained was measured from room temperature (ca. 25°C) to 50°C at a heating rate of 20°C/min. The load was 4 g and forced longitudinal vibration (sine wave) was 0.25 Hz. Moreover, the compressive moduli of the gels preserved in water, and the freeze-dried gels were also measured.

RESULTS AND DISCUSSION

Dissolution of α-PVA and Properties of Solutions

The dissolution temperature of α-PVA depended on the concentrations of saccharides and α-PVA.

Table II Dynamic Compressive Modulus of α-PVA Hydrogels With or Without Saccharides from 25 to 50°C and Transparency of Gels With Initial Saccharide Contents of 50 and 0 g/dL and an Initial Polymer Concentration of 5 g/dL

Gel	(a) As-Frozen/Thawed Gels	(b) Freeze-Dried Gels of (a)	(c) Gels of (b) Preserved in Water
Gels without saccharides	30 kPa, transparent	2-1 MPa, chalky	180 kPa, chalky + transparent
Gels with xylose	75 kPa, transparent	800 kPa, chalky	75 kPa, chalky
Gels with fructose	60 kPa, transparent	160 kPa, translucent	35 kPa, chalky
Gels with glucose	50 kPa, transparent	200 kPa, translucent	40 kPa, chalky
Gels with saccharose	40 kPa, transparent	80 kPa, translucent	45 kPa, translucent
Gels with maltose	60 kPa, transparent	170 kPa, translucent	35 kPa, chalky

Table III Dynamic Compressive Modulus of *a*-PVA Hydrogels With or Without Saccharides from 25 to 50°C and Transparency of Gels With Initial Saccharide Contents of 50 and 0 g/dL and an Initial Polymer Concentrations of 5 g/dL

Gel	(a) As-Frozen/Thawed Gels	(d) Gels of (a) Preserved in Water	(e) Freeze-Dried Gels of (d)
Gels without saccharides	30 kPa, transparent	13 kPa, transparent	3 MPa, chalky
Gels with xylose	75 kPa, transparent	30 kPa, transparent	3 MPa, chalky
Gels with fructose	60 kPa, transparent	45 kPa, cloudy	450 kPa, chalky
Gels with glucose	50 kPa, transparent	40 kPa, cloudy	3 MPa, chalky
Gels with saccharose	40 kPa, transparent	30 kPa, transparent	1.4 MPa, translucent
Gels with maltose	60 kPa, transparent	45 kPa, cloudy	530 kPa, chalky

However, in the case of any saccharides, the dissolution temperature of *a*-PVA was 79–92°C in the range of saccharide concentrations of 0–20 g/dL and the addition effect of saccharides was hardly recognized. This was considered to be due to that the free water molecules, which were not concerned with the dissolution of saccharides, existed in large quantities so that no saccharide contents influenced to the dissolution temperature of *a*-PVA. The influence was recognized in the saccharide content above 40 g/dL, and the solubility of *a*-PVA was lowered with an increase of molecular mass of saccharides. In the case of the fructose content of 60 g/dL, the dissolution temperature of *a*-PVA (polymer concentration: C = 3–12 g/dL) was 99–106°C (Fig. 1). In the case of a maltose content of 50 g/dL, it was 97–105°C (C = 3–12 g/dL).

During gradual cooling of the aqueous *a*-PVA solutions with the saccharide contents above 50 g/dL, the solutions were cloudy after gelling (Fig. 2). The gelling temperature lowered with the decrease of saccharide contents. However, the clouding temperature was the minimum in the xylose content of 30 g/dL, the maximum on the maltose content of 40 g/dL, and no clouding occurred during gradual cooling to 0°C in the glucose contents below 40 g/dL and the fructose content of 40 g/dL. Namely, the solubility of saccharides at the lower temperatures below 30°C was complicated. The aqueous *a*-PVA solutions gelled after clouding (Fig. 2).

Figure 3 shows relations between the critical polymer concentration of gelation and the content of xylose obtained by chilling at 0 and 10°C for 24 h. The critical polymer concentration of gelation lowered with the decrease of chilling temperature and with an increase of xylose content. Whichever saccharide we used, the relation was similar. None of these results coincided with the results of clouding of solutions described above.

Melting Temperature of Gels

Figure 4 shows the relations between the melting temperature and the polymer concentration for the *a*-PVA gels chilled at 0°C. The melting temperature was below 30°C for gels with saccharide contents below 20 g/dL. For the *a*-PVA gels with a saccharide content of 40 g/dL, the transition point appeared (Fig. 4). The critical *a*-PVA concentration at the transition point was about 8 g/dL for xylose (Fig. 4), 7.5 g/dL for fructose, 5.5 g/dL for glucose, and 7.5 g/dL for maltose. For the saccharides used in this article, the interrelation between those critical concentrations was not recognized. The melting temperature of hydrogels with glucose was the same as that of maltose and higher than those of xylose and fructose. Namely, the solubility of glucose into water was recognized to be the lowest at lower temperatures (0–40°C).

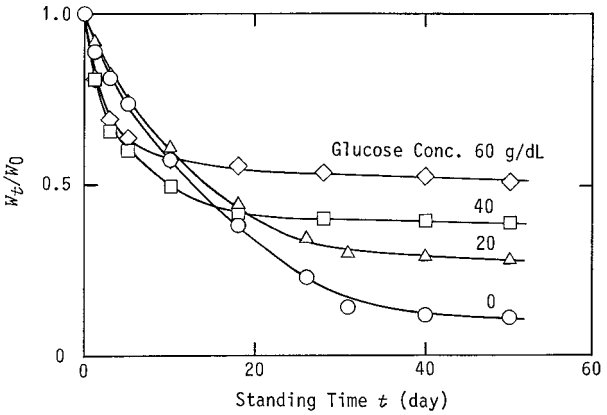

Figure 5 Change in weight of gels in air during standing at room temperature for 10 g/dL *a*-PVA hydrogels with glucose.

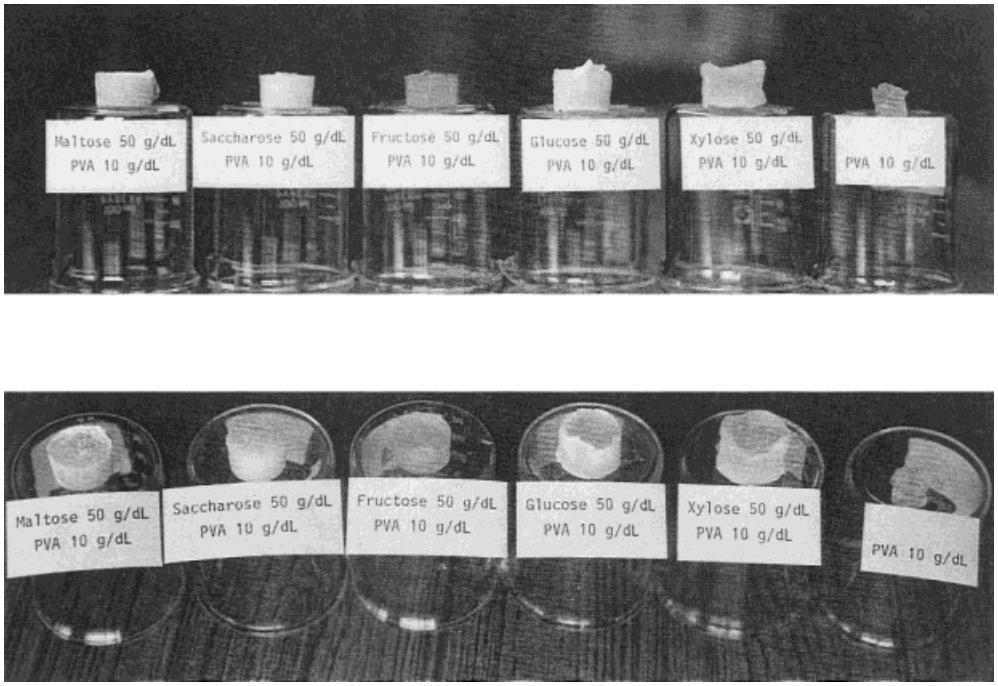

Figure 6 Photographs of gels with or without saccharides (50 or 0 g/dL) after standing for 50 days in air (initial polymer concentration: 10 g/dL).

Also, the effect of the chilling temperature on the melting temperature of gels was examined. In the region of the saccharide contents of 10–30 g/dL, the critical *a*-PVA concentration of gelation increased with an increase in the chilling temperature, and the melting temperature of gels decreased at same *a*-PVA concentration. However, in the case of gels with the saccharide contents above 50 g/dL, except gels with maltose, the effect of the chilling temperature (0–30°C) on the melting temperature was very low, and the melting temperature was nearly equal in the region of higher *a*-PVA concentrations.

The enthalpy of the thermal dissociation of the junctions of the spatial network ΔH, estimated by the Eldridge–Ferry equation, is shown in Table I. In this article, ΔH was obtained from the relations between the *a*-PVA concentration and the melting temperature for *a*-PVA gels in the range of high melting temperatures (above 60°C). Also, the result of saccharose obtained in the previous article[12] is shown. The ΔH values were independent of the molecular mass of saccharides. However, the ΔH values were the lowest for xylose and the highest for glucose and, the critical *a*-PVA concentration at the transition point, as shown in Figure 4, was reverse.

Dynamic Modulus of Gels

Tables II and III show the dynamic compressive modulus of *a*-PVA hydrogels with and without saccharides (50 or 0 g/dL) obtained after three cycles of the freezing/thawing process. All hydrogels were roughly transparent but the modulus of the gels without saccharides were higher than that of the gel with saccharides. The modulus of the hydrogels with xylose was the highest. As those gels were dried under freezing, the gels with saccharides became translucent, except the gel with xylose. Those modului increase only a very little. However, the freeze-dried gels with xylose became chalky, and the modulus increased considerably (Table II). However, the modulus was much lower than that of the freeze-dried gels without saccharides.

As the as-frozen/thawed gels were preserved in water for 24 h, the moduli of the gels decreased somewhat, especially below half for the gels without saccharides and with xylose [Table III, compared with (a) and (d)]. Namely, many unstable junctions in the gels dissolved. However, the gels of (d) were, as a whole, stable in comparison with that of the as-frozen/thawed gels without saccharides (a). It was considered that the stable junctions were reformed after dissolving the weak,

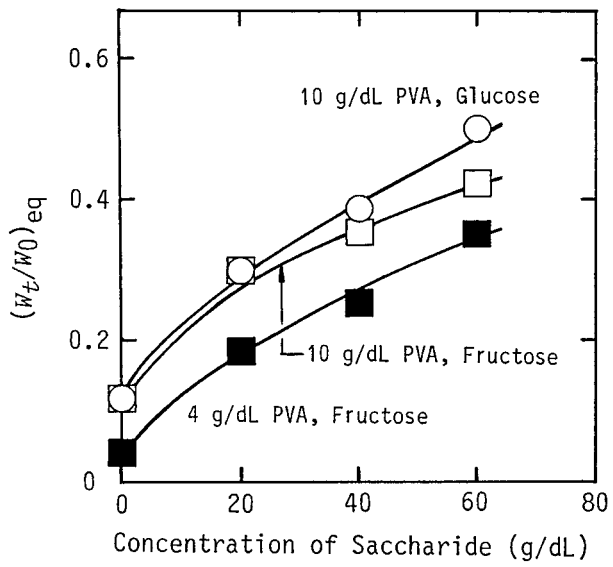

Figure 7 Relations between $(W_t/W_0)_{eq}$ and concentration of saccharides for 4 or 10 g/dL α-PVA hydrogels with glucose or fructose.

unstable junctions. During refreeze-drying of those gels, the mechanically stable junctions increased, and those moduli rose to 1.4–3 MPa, except the gels with fructose and maltose. Namely, in the case of the gels with fructose and maltose, it is expected that water still considerably remains in the gels of (e) after freeze-drying. The fact shows that fructose and maltose molecules were reserved in the gels even after standing in water for a long time.

Syneresis of Gels

Figure 5 shows the relations between W_t/W_0 and the standing time for 10 g/dL α-PVA hydrogels with glucose. W_0 is the weight of gels after three cycles of freezing/thawing, and W_t is that of gels after standing in air for t days. W_t/W_0 decreased rapidly with an increase in the standing time for the gels with glucose contents of 40–60 g/dL, and it gradually approached the fixed value after standing for 20 days. In the case of other saccharides, the similar tendency was recognized. An example of gels with and without saccharose (50 and 0 g/dL) after standing for 50 days is shown in Figure 6 (initial polymer concentration: 10 g/dL).

In the gels with xylose and glucose, the crownlike forms were recognized. In the saccharide/water gels which reached equilibrium, the inside was flexible, whereas the outside was rigid, except equilibrium gels with fructose. Figure 7 shows the relations between the W_t/W_0 value at equilibrium, $(W_t/W_0)_{eq}$, and the saccharide concentration. As the equilibrium gel with fructose was more flexible than the equilibrium gel with glucose, the surface of the former was sticky, and the surface of latter was not, it was considered that the former had more water than the latter. However the expectation comes off, the $(W_t/W_0)_{eq}$ value for gels with fructose was lower than that for gels with glucose. It is considered that the solidification of surface for gels with glucose interferes with the transportation of water molecules to the gel surface; that is, the affinity of water and glucose molecules is lower than that of water and fructose.

A part of this work was supported by Grant-in-Aid for COE Research (10CE2003) by the Ministry of Education, Science, Sports and Culture of Japan.

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