ELSEVIER

Carbohydrate Polymers 46 (2001) 373–381

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Viscoelastic properties of plasticized methylcellulose and chemically crosslinked methylcellulose

J.-S. Park[a], E. Ruckenstein[b,*]

[a]Department of Chemical Engineering, Hankyong National University, Ansung, Kyunggi-do 456-749, South Korea
[b]Department of Chemical Engineering, State University of New York at Buffalo, Furnas Hall, Amherst, NY 14226, USA

Received 13 July 2000; revised 7 November 2000; accepted 8 November 2000

Abstract

Films of methylcellulose (MC), poly(ethylene glycol)400 (PEG400) plasticized MC, and MC gels (MC crosslinked with glutaraldehyde (GA)) were prepared by casting from aqueous solutions. The swelling test has shown that the MC gels were insoluble in water and that their crosslinking density increased with increasing GA and HCl concentrations. The effect of the addition of PEG400 or GA to MC was investigated through dynamic mechanical analysis (DMA). The DMA analysis of PEG400/MC blends has shown that PEG400 was compatible with MC and was an effective plasticizer since the curves of tan δ against temperature exhibited single peaks (corresponding to a single glass transition temperature), which were displaced to lower values with increasing PEG400 content. The thermogravimetric analysis (TGA) indicated that the thermal stability of MC was not affected by the chemical crosslinking. The tensile strength was slightly increased through crosslinking while the elongation was slightly decreased. The presence of moisture in MC hydrogels decreased the tensile strength and enhanced the elongation while the addition of PEG400 decreased the tensile strength but sharply increased the elongation.

Keywords: Methylcellulose; Chemical crosslinking; Dynamic mechanical analysis; Poly(ethylene glycol)400; Gel; Miscibility

1. Introduction

Cellulose constitutes the main structural component of plants and the most abundant source of carbohydrate in nature (BeMiller, 1986). Because of its highly crystalline nature, it is insoluble and unswellable in water. In order to solubilize cellulose, various substituents have been incorporated into its anhydroglucose backbone to decrease its crystallinity. In methylcellulose (MC), some hydroxyls are replaced with methoxyl groups and thus the hydrogen-bonding, which is responsible for the crystallinity of cellulose, is weakened. For this reason MC becomes water soluble. MC is prepared on a commercial scale by the etherification of alkali-cellulose with methyl chloride (BeMiller, 1986). The degree of substitution (DS), i.e. the number of substituted hydroxyl groups per anhydroglucose unit, ranges from 1.6 to 1.9 in the commercially water-soluble products. The properties of MC depend on both the DS and the distribution of the substituents along the cellulose backbone (Arisz, Kauw & Boon, 1995; Desbrieres, Hirrien & Ross-Murphy, 2000; Hirrien, Chevillard, Desbrieres & Rinaudo, 1998; Hirrien, Desbrieres & Rinaudo, 1996; Sarkar & Walker, 1995). MC provides high-strength films that are transparent, water soluble, and oil- and grease resistant, and have low oxygen and moisture vapor transmission rates (BeMiller, 1986; Park, Weller, Vergano & Testin, 1993; Rico-Pena & Torries, 1990). These biodegradable and edible films have attracted increasing interest in recent years because they can be used as packing materials (Park et al., 1993; Rico-Pena & Torries, 1990). A major component of these biopolymer films is the plasticizer which helps to overcome the brittleness (Arvanitoyannis & Biliaderis, 1999; Arvanitoyannis, Psomiadou, Nakayama & Yamamoto, 1997; Beck & Tomika, 1996; Goswami & Maiti, 1998; Liang, Guo, Gu & Ding, 1995; Liu, Khang, Rhee & Lee, 1999). The plasticizers decrease the intermolecular interactions among the functional groups of the backbone chains, thus increasing the mobility of the chains, resulting in increased flexibility and extensibility. In the agriculture and food industry, glycol plasticizers are used for MC products for rolling, casting, or extruding them into films. Among various plasticizers for MC, the polyethylene glycols (PEG) have certain advantages (Arvanitoyannis & Biliaderis, 1999; Arvanitoyannis et al., 1997; Chun & Park, 1999; Goswami

* Corresponding author. Tel.: +1-716-645-2911, ext. 2214; fax: +1-716-645-3822.
E-mail address: feaeliru@acsu.buffalo.edu (E. Ruckenstein).

0144-8617/01/$ - see front matter
PII: S0144-8617(00)00336-2

Table 1
Amount of water uptake by the MC gel film as a function of the concentration of the crosslinker. The concentration of HCl was 2.25×10^{-1} mol/l. The gel film was dried in a vacuum oven for 3 h at 100°C (Sol: soluble in water)

Concentration of GA (mol/l)	Water content in gel (W_c) (g/g)
0	Sol
6.3×10^{-4}	Sol
2.5×10^{-3}	Sol
5.0×10^{-3}	Sol
8.4×10^{-3}	0.56
1.7×10^{-2}	0.54

& Maiti, 1998; Liang et al., 1995; Liu et al., 1999) because they provide a higher plasticity than other small molecular weight molecules, such as glycerol and sorbitol, possess some hygroscopicity that helps in retaining a moderate moisture in the polymer, and improve the flexibility without sacrificing much of the tensile strength. In addition, PEG is soluble in most of the polar solvents and is miscible with hydrophilic polymers. The films plasticized with PEG absorb some moisture because the terminal hydroxyl groups and the ether groups of PEG are hydrophilic. The presence of this moisture in MC has significant effects on its physical properties, especially on the mechanical properties, because it plasticizes the biopolymer by interfering with the hydrogen-bonding between the hydroxyl groups of MC (Nokhodchi, Ford & Rubinstein, 1997; Sarkar & Walker, 1995). MC gels can be prepared by reacting some of its hydroxyl groups with the aldehyde groups of glutaraldehyde (GA) in the presence of an acid.

Most of the experimental work reported in the literature was dedicated to the thermogelation of MC solutions (Desbrieres, Hirrien & Rinaudo, 1998; Desbrieres et al., 2000; Hirrien et al., 1998). In this paper, the thermal and viscoelastic properties of films of MC, poly(ethylene glycol)400 (PEG400) plasticized MC, and MC gel were investigated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

MC (M_n about 17,000 with 27.5–31.5 wt% methoxy and DS of methoxy 1.6–1.9) and GA (25 wt% aqueous solution) were purchased from Aldrich Chem. Co. and PEG (M_w 300–10,000) from Yukuri Pure Chem. (Japan), and used without further purification. The solvents used were of analytical grade and the water was double distilled.

2.2. Film preparation

The MC gels were prepared by crosslinking MC with GA. MC was dissolved in water with constant stirring to obtain a 5 wt% solution. The polymer solutions were cooled to room temperature and then GA and HCl were added for crosslinking. Films were prepared by casting on a glass plate. To eliminate the insoluble impurities, the polymer solutions were glass filtered before casting. Films of 50–80 μm were obtained by drying at room temperature for 72 h. The PEG plasticized MC films were prepared by introducing the plasticizer into the polymer solution, followed by casting. Several molecular weights of PEG were employed, ranging from 300 to 10,000. Compared to PEG400, there were, however, only small decreases in the miscibility and tensile strength of the plasticized MC when PEG10,000 was employed. For this reason, only the results obtained with PEG400 are presented in the paper.

2.3. Swelling test of the gel films

The water content of the gel films after swelling was calculated using the expression

$$W_c = (W_s - W_d)/W_d,$$

where W_c is the water uptake in grams per gram of dried gel film, and W_s and W_d are the weights of the gel film after swelling and after subsequent drying, respectively. The time duration for swelling was 24 h. The excess water present on the surface of the swollen films was wiped out with a filter paper.

2.4. Instrumentations

The DMA was conducted using a DMA 2980 instrument (TA Instruments) in the tensile mode, at a frequency of 1 Hz, by heating from −120 to 260°C at a rate of 2°C/min in a nitrogen atmosphere. The cast films, with dimensions of about $3 \times 10 \times 0.05$ mm, were subjected to sinusoidal deformations with a 5 μm amplitude. The thermal behavior was examined with a TG/DTA 6200 instrument (Seiko Instruments Co., Japan) by heating from room temperature up to 750°C at a heating rate of 20°C/min under a nitrogen flow. The mechanical properties of the films were determined using a texture analyser (Stable Micro System, UK). The samples for the tensile test were prepared in two different ways: one was by conditioning in a 50% relative humidity atmosphere for 48 h and the other was by drying at 100°C in a vacuum oven for 3 h. The tensile strength and the elongation of the films were determined at an extension rate of 500 mm/min, at room temperature.

3. Results and discussion

3.1. Swelling measurements

The solid films of MC, PEG400 plasticized MC, and MC gel, prepared by casting from aqueous solutions, were transparent, homogeneous, and possessed moderate mechanical strengths. Particularly, the plasticized films exhibited increased transparency and flexibility with increasing

Table 2
Amount of water uptake by the MC gel film as a function of the concentration of the catalyst (HCl). The concentration of the crosslinker was 2.25×10^{-1} mol/l. The gel film was dried in a vacuum oven for 3 h at 100°C (Sol: soluble in water)

Concentration of HCl (mol/l)	Water content in gel (W_c) (g/g)
0	Sol
7.0×10^{-3}	Sol
1.0×10^{-2}	0.81
2.8×10^{-2}	0.73
1.1×10^{-1}	0.58
2.3×10^{-1}	0.56

PEG400 content. While the MC and plasticized MC films were soluble in water, the MC gel films became insoluble for sufficiently high crosslinking densities. Tables 1 and 2 provide information about the swelling of the MC gels prepared with various crosslinker and catalyst concentrations. The water uptake of the MC gels, which is a measure of their degree of crosslinking, decreased with increasing GA and HCl concentrations. This indicates that the hydroxyl groups of the MC backbone were chemically crosslinked with GA, forming a three-dimensional MC insoluble in water. Tables 1 and 2 show that lightly crosslinked MC gels, prepared with GA concentrations less than 5.0×10^{-3} mol/l and HCl concentrations less than 1.0×10^{-2} mol/l, became soluble. As expected, the highly crosslinked MC was less swellable in water.

3.2. Dynamic mechanical analysis

The DMA constitutes a sensitive tool for the detection of the molecular relaxations of a polymer and leads to information about the molecular structure of the polymer. The results of the dynamic mechanical measurements for the MC films are presented in Figs. 1–3. Fig. 1 provides the temperature dependence of tan δ and storage modulus E' of an MC film in the temperature range of −120 to 260°C. Three relaxation peaks γ, β, and α can be observed in the tan δ curve at −91.0, 26.8, and 199.5°C, respectively. The relaxation peak at 199.5°C corresponds to the glass transition of MC, around which the storage modulus (E') decreases markedly. This result can be contrasted with that obtained for cellulose, for which a glass transition temperature could not be detected via the DMA before thermal degradation took place (Nishio & Manley, 1987, 1988). The polymers which contain hydroxyl groups are hydrophilic and interact with water. Moisture plasticizes the hydrophilic polymers by interfering with the hydrogen bonds among the hydroxyl groups of the polymer molecules (Gimenez, Mantecon & Cadiz, 1996; Hodge, Edward & Simon, 1996; Sarkar & Walker, 1995). Fig. 2 plots the temperature dependence of tan δ and E' for MC and wet MC (ca. 5 wt% water in polymer), respectively. There is no discernable difference in the tan δ curves of the two, appearing to indicate that water did not exert any plasticizing effect on MC. However, this occurred because the water vaporized

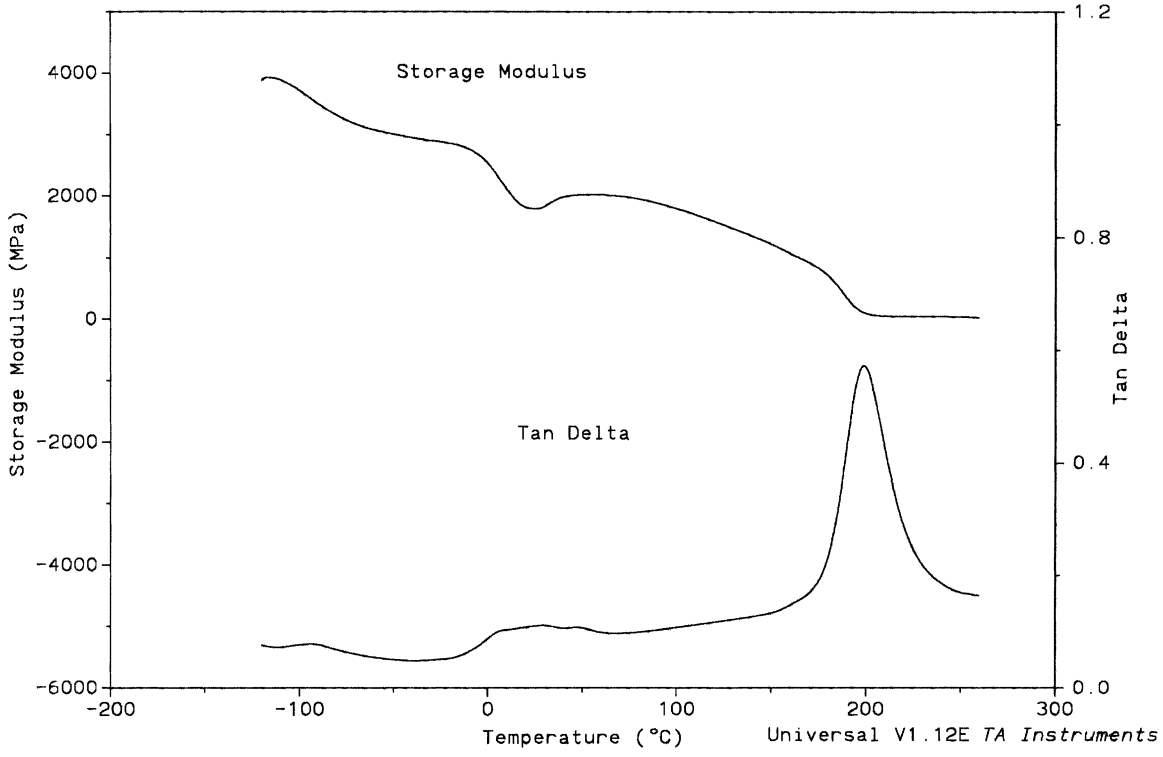

Fig. 1. Temperature dependence of storage modulus and tan δ for MC. The determinations were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude.

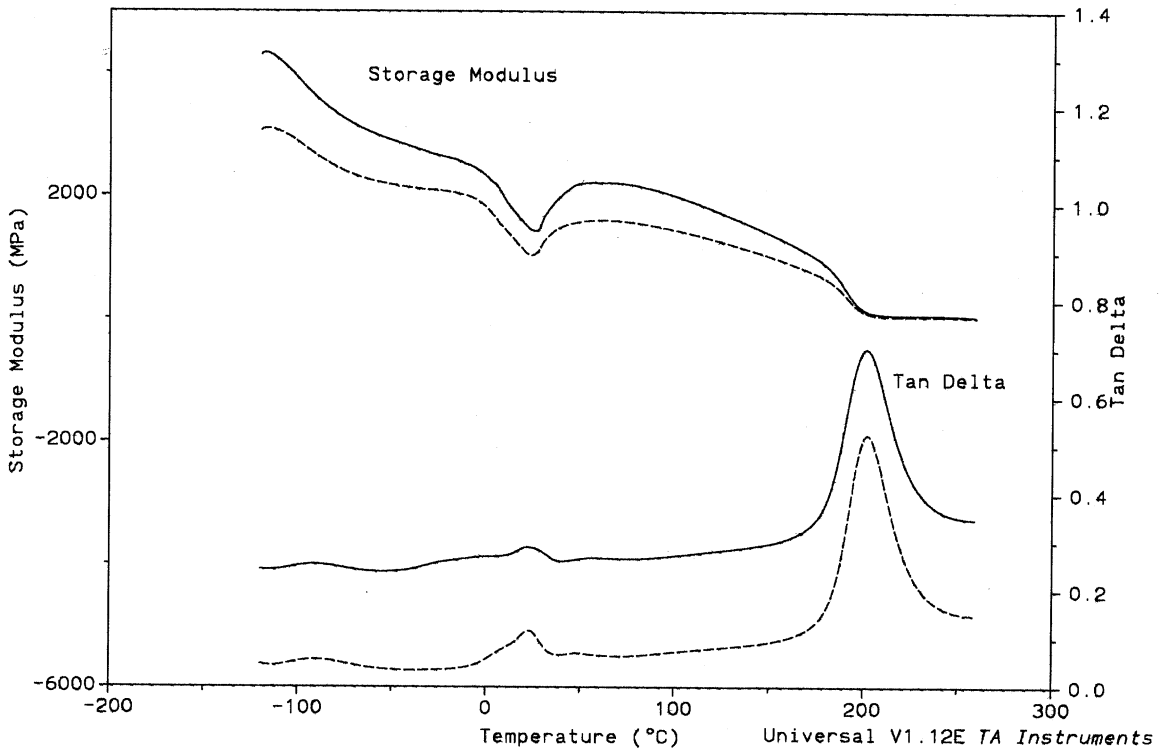

Fig. 2. Temperature dependence of the storage modulus E' and tan δ for: (—), MC and (- - - -), moisture containing MC. The determinations were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude under nitrogen.

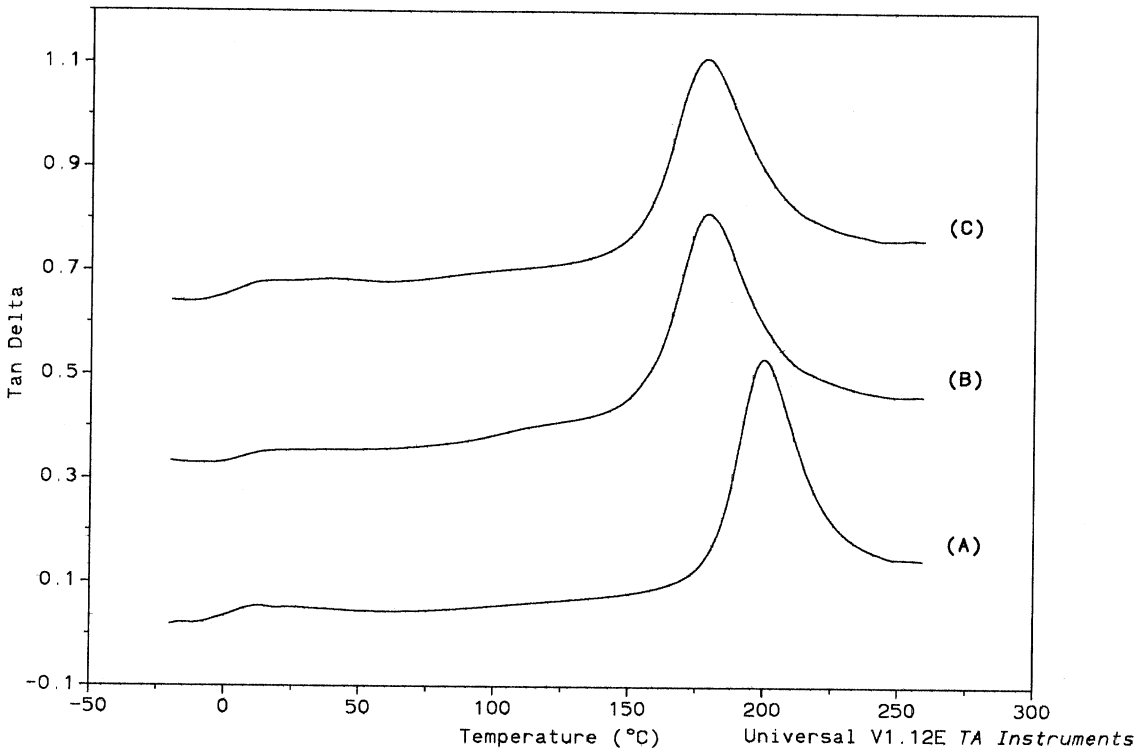

Fig. 3. Temperature dependence of tan δ for: (A) MC; (B) PEG400 plasticized MC; and (C) moisture and PEG400 containing MC. The glutaraldehyde and HCl concentrations employed to prepare the hydrogel were 8.38×10^{-3} mol/l and 2.25×10^{-1} mol/l, respectively. The determinations were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude under nitrogen.

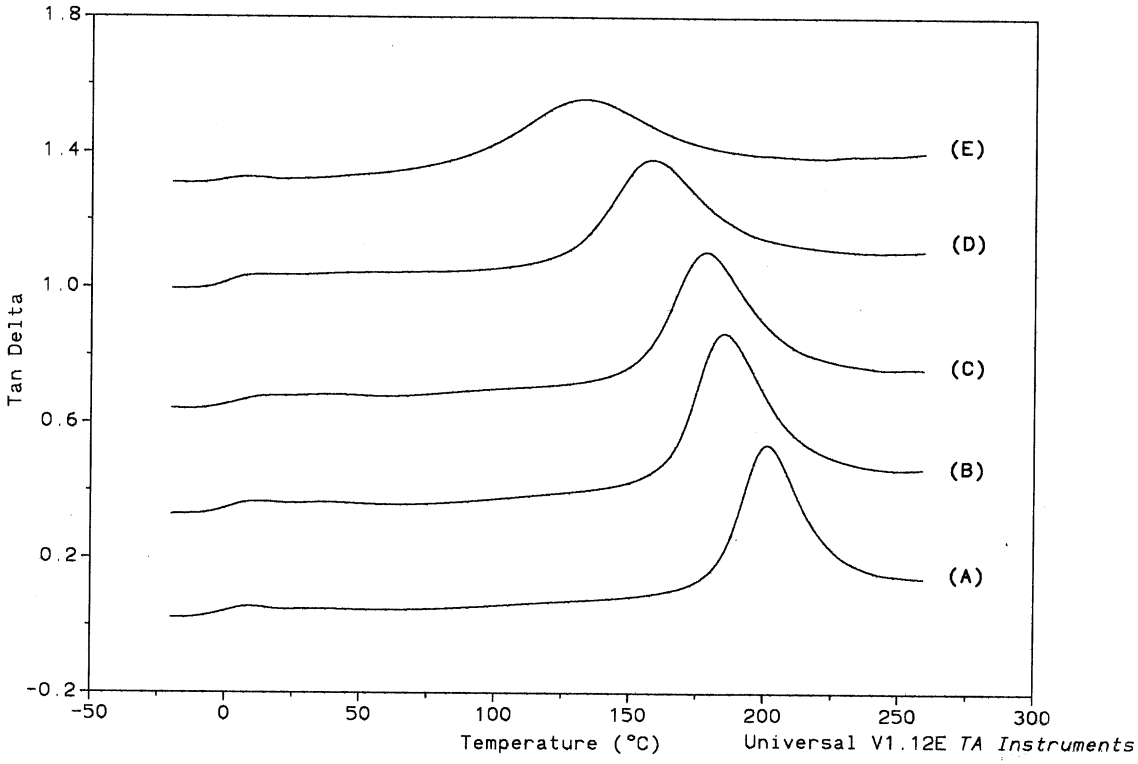

Fig. 4. Temperature dependence of tan δ for MC and PEG400 plasticized MC. The content of PEG400: (A) 0 wt%; (B) 2.0 wt%; (C) 7.0 wt%; (D) 14.0 wt%; and (E) 24.0 wt%. The determinations were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude under nitrogen.

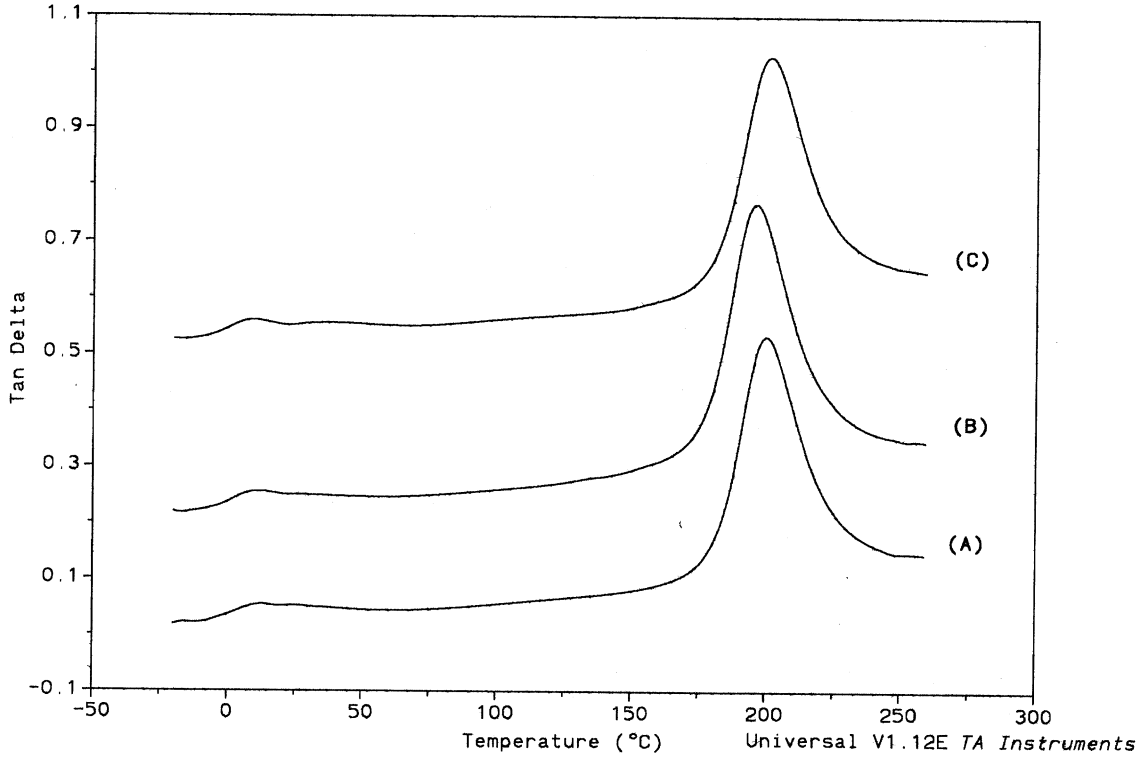

Fig. 5. Temperature dependence of tan δ for: (A) MC; (B) MC gel; and (C) moisture containing MC gel. The GA and HCl concentrations employed to prepare the MC gel were 8.38×10^{-3} mol/l and 2.25×10^{-1} mol/l, respectively. The determinations were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude under nitrogen.

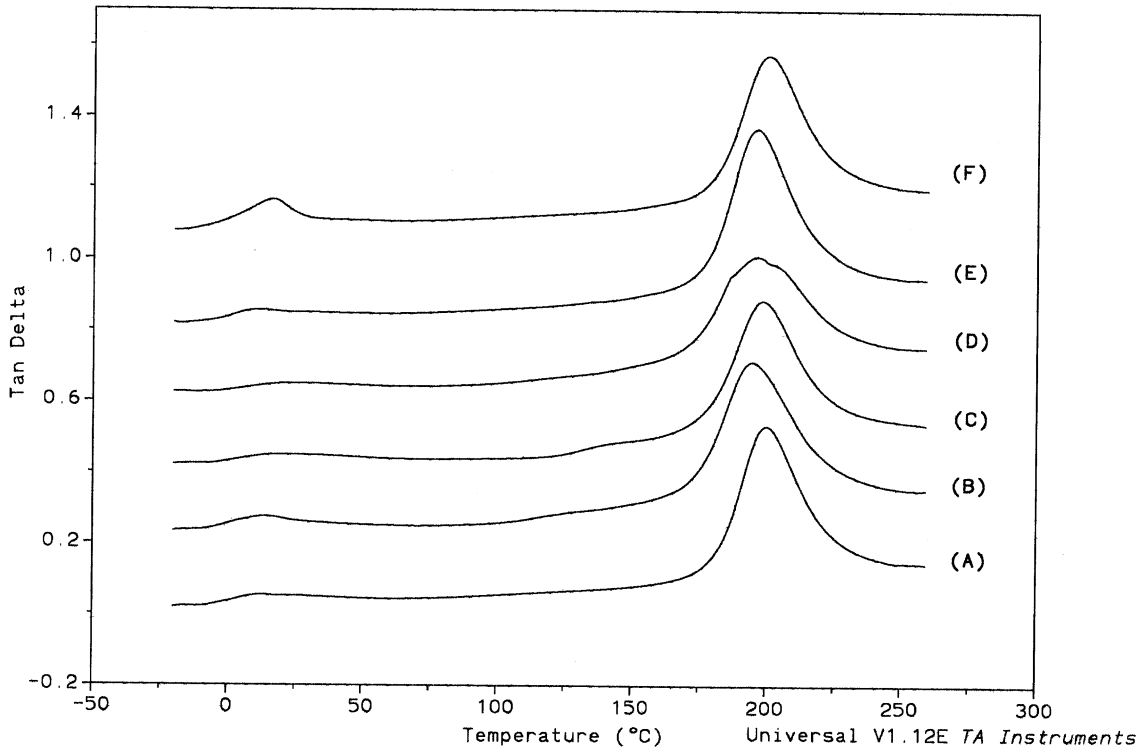

Fig. 6. Temperature dependence of tan δ for MC gels prepared by changing the concentration of GA. The concentration of GA: (A) 0 mol/l; (B) 6.3×10^{-4} mol/l; (C) 2.5×10^{-3} mol/l; (D) 5.0×10^{-3} mol/l; (E) 8.4×10^{-3} mol/l; and (F) 1.7×10^{-2} mol/l. The determinations were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude under nitrogen.

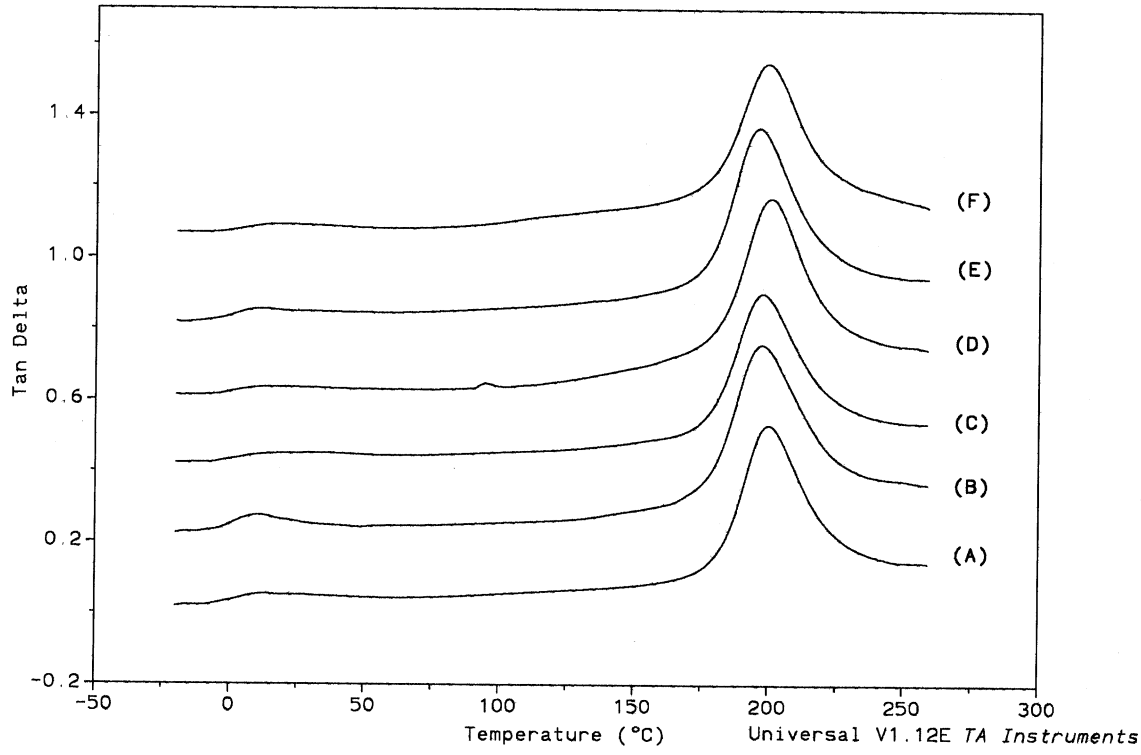

Fig. 7. Temperature dependence of tan δ for MC gels prepared by changing the concentration of HCl. The concentration of HCl: (A) 0 mol/l; (B) 7.0×10^{-3} mol/l; (C) 1.0×10^{-2} mol/l; (D) 2.8×10^{-2} mol/l; (E) 1.1×10^{-1} mol/l; and (F) 2.3×10^{-1} mol/l. The concentration of GA was 8.38×10^{-3} mol/l. The measurements were conducted at 2°C/min heating rate, 1 Hz frequency, and 5 μm amplitude under nitrogen.

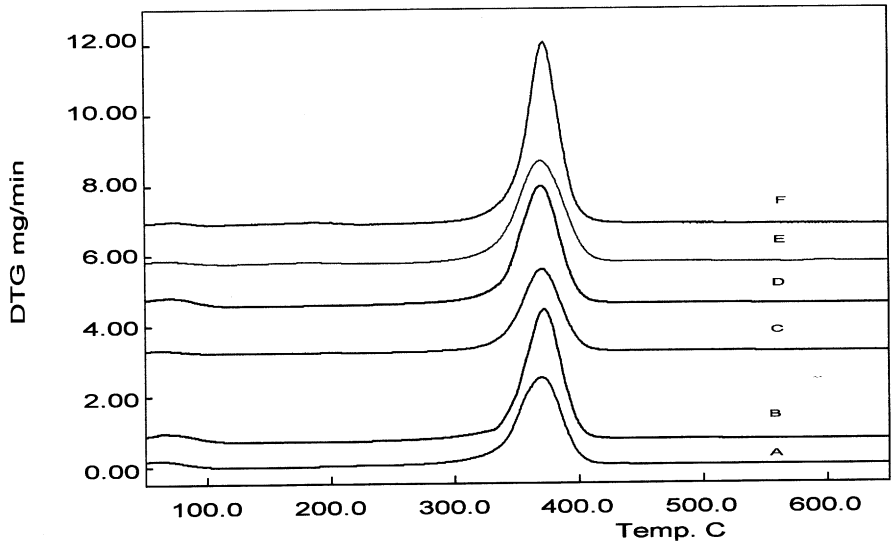

Fig. 8. Differential thermogravimetric (DTG) thermograms of MC gels prepared by changing the concentration of GA. The concentration of GA: (A) 0 mol/l; (B) 6.3×10^{-4} mol/l; (C) 2.5×10^{-3} mol/l; (D) 5.0×10^{-3} mol/l; (E) 8.4×10^{-3} mol/l; and (F) 1.7×10^{-2} mol/l. The concentration of HCl was 2.25×10^{-1} mol/l. The determinations were conducted at 2°C/min heating rate under nitrogen.

before MC reached the glass transition temperature of 199.5°C. Fig. 3 presents the temperature dependence of tan δ for MC, PEG400 plasticized MC, and wet PEG400 plasticized MC. The results indicate that PEG acted as a plasticizer for MC because it provided a large decrease of the glass transition temperature. Fig. 3 also shows that moisture had no effect on the glass transition temperature of the plasticized MC. Fig. 4 presents the temperature dependence of tan δ for plasticized MC, at various concentrations of PEG400, in the temperature range of -20 to 260°C; it shows that the glass transition temperature of MC decreased sharply with increasing plasticizer content. The FT-IR results of Liang et al. (1995) brought evidence that there are hydrogen bonds between the hydroxyl groups of PEG400 and those of MC. These bonds decrease the intermolecular interactions between the MC chains, which thus become more flexible. Fig. 5 presents the temperature dependence of tan δ for MC, MC gel, and wet MC gel. The hydroxyl groups of the anhydroglucose unit of MC reacted with the dialdehyde groups of GA generating a three-dimensional crosslinked structure. There was no decrease in the glass transition temperature of MC after chemical crosslinking. This indicates that the MC backbone was so rigid that the glass transition temperature of MC gel did not change

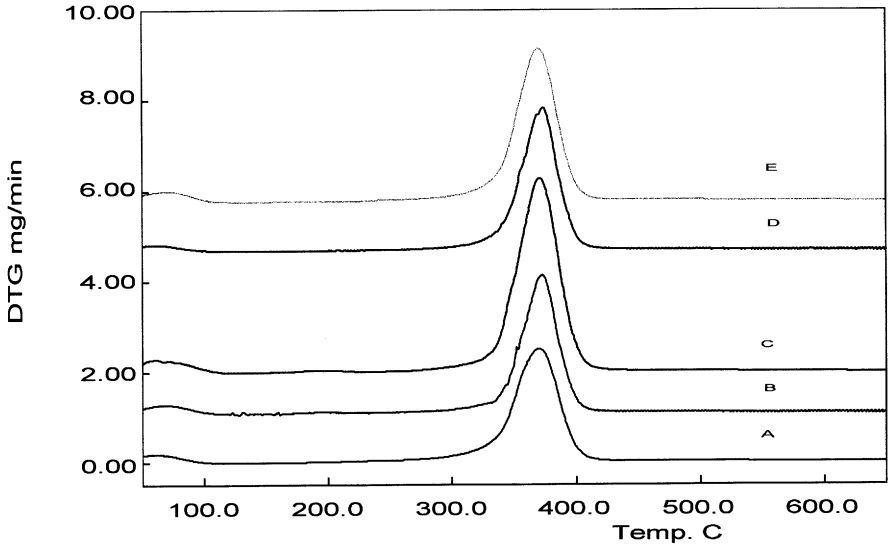

Fig. 9. Differential thermogravimetric (DTG) thermograms of MC gels prepared by changing the concentration of HCl. The concentration of HCl: (A) 0 mol/l; (B) 7.0×10^{-3} mol/l; (C) 1.0×10^{-2} mol/l; (D) 2.8×10^{-2} mol/l; and (E) 1.1×10^{-1} mol/l. The concentration of GA was 8.38×10^{-3} mol/1. The determinations were conducted at 20°C/min heating rate under nitrogen.

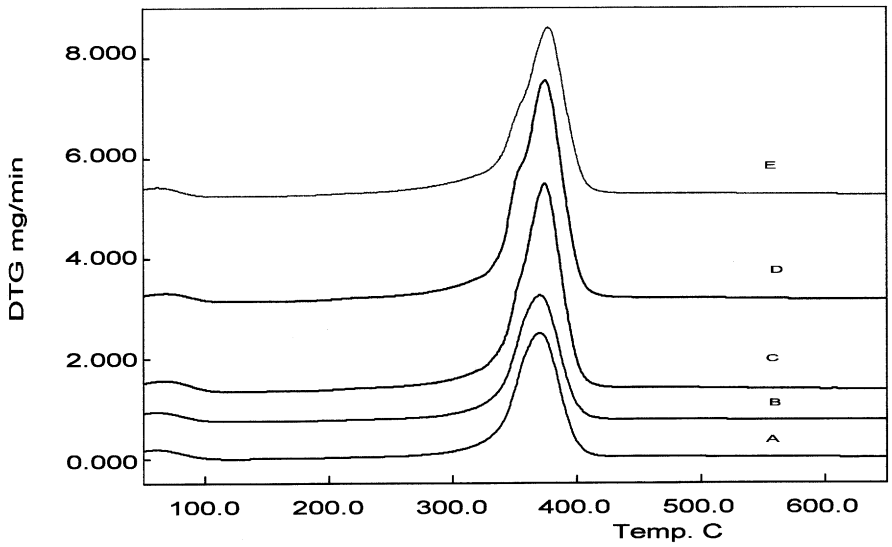

Fig. 10. Differential thermogravimetric (DTG) thermograms of PEG400 plasticized MC. The content of PEG400: (A) 0 wt%; (B) 2.0 wt%; (C) 7.0 wt%; (D) 14.0 wt%; and (E) 24.0 wt%. The determinations were conducted at 20°C/min heating rate under nitrogen.

after crosslinking. No effect of moisture on the glass transition temperature of MC and MC gel could be detected because of its loss during scanning. Figs. 6 and 7 present the temperature dependence of tan δ for MC gels prepared by changing the concentration of the catalyst and of the crosslinker, respectively. The MCs and the MC gels exhibited almost the same glass transition temperatures, indicating that the effect of crosslinking was negligible.

3.3. TGA analysis

The thermal degradations of MC, PEG400 plasticized MC, and MC gel were investigated by TGA. The derivatives of the thermogravimetric curves are presented in Figs. 8 and 9. A slight weight decrease of MC started below 100°C, due to the loss of moisture, and a large decrease took place in the temperature range of 332–395°C, with a peak at 373°C, because of the structural degradation of MC. In general, the thermal stability of a polymer is improved by crosslinking (Aoi, Yakasu, Tsuchiya & Okada, 1998). However, in the present case, the thermal stability of the MC gels remained comparable to that of the unmodified MC (Figs. 8 and 9) because of the rigid anhydroglucose unit of MC. Fig. 10 presents the DTG curves for MC and for PEG400 plasticized MC. These curves possess single peaks and the peak for the latter is shifted slightly to a higher temperature. This indicates that MC and PEG400 are compatible and that the thermal stability of plasticized MC is improved compared to that of MC.

3.4. Tensile test

Tables 3 and 4 list the tensile strength and percentage

Table 3
The tensile strength and elongation of wet MC gels and dried MC gels were determined at an extension rate of 500 mm/min at room temperature. The films of wet MC gels were conditioned in a 50% relative humidity atmosphere at room temperature for 48 h while the films of dried MC gels were dried in a vacuum oven at 100°C for 3 h. The gels were prepared at various concentrations of the crosslinker and a concentration of HCl of 2.3×10^{-1} mol/l

Concentration of GA (mol/l)	Wet MC gels		Dried MC gels	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0	48.0	2.5	67.3	1.6
6.3×10^{-4}	49.2	2.3	70.2	1.4
2.5×10^{-3}	50.8	2.0	72.5	1.1
5.0×10^{-3}	51.7	1.5	73.1	1.0
8.4×10^{-3}	52.1	1.4	73.5	0.8
1.7×10^{-2}	52.3	1.4	74.7	0.8

Table 4
Tensile strength and elongation of wet MC gels and dried MC gels were measured at an extension rate of 500 mm/min at room temperature. The films of wet MC gels were conditioned in a 50% relative humidity atmosphere at room temperature for 48 h while the films of dried MC gels were dried in a vacuum oven at 100°C for 3 h. The gels were prepared at various concentrations of HCl and a concentration of GA of 8.4×10^{-3} mol/l

Concentration of HCl (mol/l)	Wet MC gels		Dried MC gels	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0	48.0	2.5	67.3	1.6
7.0×10^{-3}	50.9	2.3	68.9	1.1
1.0×10^{-2}	51.2	2.0	69.5	1.0
2.8×10^{-2}	52.0	1.5	70.2	1.0
1.1×10^{-1}	52.0	1.4	71.2	0.9
2.3×10^{-1}	52.1	1.4	73.5	0.7

Table 5
The tensile strength and elongation of wet MC and dried MC were determined at an extension rate of 500 mm/min at room temperature. The films of wet MC were conditioned in a 50% relative humidity atmosphere at room temperature for 48 h while the films of dried MC were dried in a vacuum oven at 100°C for 3 h

Amount of PEG400 added to MC (wt%)	Wet MC		Dried MC	
	Tensile stregth (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0	48.0	2.5	67.3	1.6
2	46.5	11.2	57.0	8.5
3.8	45.1	14.6	51.8	11.5
7.4	44.3	17.1	46.6	14.3
13.8	33.5	25.1	36.7	16.5

elongation of the MC gels, prepared with various concentrations of crosslinker and catalyst. The tensile strength of the MC gels increased with increasing GA and HCl concentrations, while the elongation decreased. The wet MC gels, conditioned in a 50% relative humidity atmosphere for 48 h, had lower tensile strengths and higher elongations than the vacuum-dried MC gels. This confirms that water plasticized the polymer backbone of the gels, thus decreasing the tensile strength and increasing the elongation. Table 5 presents the effect of PEG400 on the mechanical properties and shows that with increasing PEG400 content the tensile strength decreased, while the elongation increased. The PEG400 plasticized the MC conditioned in 50% relative humidity atmosphere for 48 h, providing lower tensile strengths and higher elongations than those for vacuum-dried and PEG400 plasticized MC, indicating a combined effect of water and PEG400 as plasticizers.

4. Conclusions

MC was chemically crosslinked with GA in the presence of HCl and thus became insoluble in water. As expected, the crosslinking density in the MC gels increased with increasing GA and HCl concentrations. Compared to MC, no discernable changes in the glass transition temperature of the MC gels, determined by DMA, were observed, indicating that the anhydroglucose unit of MC was very rigid and that the crosslinking of its hydroxyl groups with the dialdehyde groups of GA had a negligible effect from this point of view. The tan δ–temperature curve, which exhibited a single peak which shifted to lower temperatures with increasing PEG400 content, indicated that PEG400 and MC are compatible. PEG400 was found to be a very effective plasticizer because it appreciably lowered the glass transition temperature. The TGA curves indicated that the thermal stability of MC remained unaffected by crosslinking and that PEG400 was compatible with MC because the curves exhibited single peaks. The tensile strength of the MC gels was slightly increased by crosslinking while their elongation was slightly decreased.

References

Aoi, K., Yakasu, A., Tsuchiya, M., & Okada, M. (1998). *Macromolecular Chemistry and Physics*, *199*, 2805.

Arisz, P. W., Kauw, H. J. J., & Boon, J. J. (1995). *Carbohydrate Research*, *271*, 1.

Arvanitoyannis, I., & Biliaderis, C. G. (1999). *Carbohydrate Polymers*, *38*, 47.

Arvanitoyannis, I., Psomiadou, E., Nakayama, A., & Yamamoto, N. (1997). *Food Chemistry*, *60*, 593.

Beck, M. I., & Tomika, I. (1996). *Macromolecules*, *29*, 8759.

BeMiller, J. N. (1986). *Encyclopaedia of polymer science and engineering*, Vol. 7. New York: Wiley (pp. 601).

Chun, D. H., & Park, J. W. (1999). *Journal of the Korean Society of Packaging Science and Technology*, *5*, 6.

Desbrieres, J., Hirrien, M., & Rinaudo, M. (1998). *Carbohydrate Polymers*, *37*.

Desbrieres, J., Hirrien, M., & Ross-Murphy, S. B. (2000). *Polymer*, *41*, 2451.

Gimenez, V., Mantecon, A., & Cadiz, V. (1996). *Journal of Polymer Science, Part A*, *34*, 925.

Goswami, T. H., & Maiti, M. M. (1998). *Polymer Degradation and Stability*, *62*, 447.

Hirrien, M., Chevillard, C., Desbrieres, J., & Rinaudo, M. (1998). *Polymer*, *39*, 6251.

Hirrien, M., Desbrieres, J., & Rinaudo, M. (1996). *Carbohydrate Polymers*, *31*, 243.

Hodge, R. M., Edward, G. H., & Simon, G. P. (1996). *Polymer*, *37*, 1371.

Liang, X. H., Guo, Y. Q., Gu, L. Z., & Ding, E. Y. (1995). *Macromolecules*, *28*, 6551.

Liu, L., Khang, G., Rhee, J. M., & Lee, H. B. (1999). *Korea Polymer Journal*, *7*, 289.

Nishio, Y., & Manley, R. St. J. (1987). *Polymer*, *28*, 1385.

Nishio, Y., & Manley, R. St. J. (1988). *Macromolecules*, *21*, 1270.

Nokhodchi, A., Ford, J., & Rubinstein, M. H. (1997). *Journal of Pharmaceutical Sciences*, *86*, 608.

Park, H. J., Weller, C. L., Vergano, P. J., & Testin, R. F. (1993). *Journal of Food Science*, *58*, 1361.

Rico-Pena, D. C., & Torries, J. A. (1990). *Journal of Food Science*, *55*, 1468.

Sarkar, N., & Walker, L. C. (1995). *Carbohydrate Polymers*, *27*, 177.