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Thermal and dynamic mechanical analysis of PVA/MC blend hydrogels

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Abstract

New blend hydrogels based on poly(vinyl alcohol) (PVA) and methylcellulose (MC) were prepared by crosslinking in an aqueous solution with glutaraldehyde (GA) in the presence of HCl. The state of the miscibility of the blend hydrogel films was examined over the entire composition range by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Depressions of the melting and crystallization temperatures of PVA were observed with increasing MC content and crosslinking density via the DSC. The determination of the glass transition temperature of blend hydrogels by DMA indicated that they exhibit a higher miscibility than the non-crosslinked blends.

Keywords: Poly(vinyl alcohol); Methylcellulose; Blend

1. Introduction

Polymer blending constitutes a most useful method for the improvement or modification of the physicochemical properties of polymeric materials. Some of the polymer blends exhibit unusual properties, unexpected from homopolymers. An important property of a polymer blend is the miscibility of its components, because it affects the mechanical properties, the morphology, its permeability and degradation [1,2]. Numerous investigations regarding the miscibility in multi-component polymer systems have been carried out. Among them, the blends between biopolymers and synthetic polymers are of particular significance because they can be used as biomedical and biodegradable materials [3–13].

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer, employed in practical applications because of its easy preparation, excellent chemical resistance and physical properties, and because it is completely biodegradable [14]. Although PVA has good mechanical properties in the dry state, its high hydrophilicity limits its applications [14–16]. However, by crosslinking one can affect its hydrophilicity [17–24]. PVA can generate a physical hydrogel by freeze–thaw cycles [17,18] and a chemical hydrogel by the chemical reaction of its hydroxyls with a crosslinker [19–21]. It can also form hydrogels through its complexation with inorganic ions, such as the borate ions [22–24]. PVA was chemically modified by using aldehydes, carboxylic acids, anhydrides, and thus its hydrophilicity, thermal and mechanical properties could be modified. The chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications, because of their permeability, biocompatibility and biodegradability [25–28].

Cellulose, an abundant natural carbohydrate, is not soluble or swellable in water. Its high rigidity and insolubility in most solvents are due to the hydroxyl groups of the anhydroglucose units, which form strong hydrogen bonds which are responsible for its crystallinity. To solubilize the crystalline cellulose, hydrophobic groups such as methyl or hydroxypropyl moieties are introduced in the cellulose backbone [29–34]. In methylcellulose (MC), one of the best known modified cellulose, some of the hydroxyl groups are replaced by methoxyl groups. MC can be prepared by reacting alkali cellulose with methyl chloride [29]. The conversion of some of the hydroxyl groups of cellulose into hydrophobic substitutients attenuates the hydrogen bonding, thus decreasing the crystallinity and increasing the water solubility. Being a polyhydroxy polymer, MC can be chemically crosslinked with a dialdehyde in the presence of a strong acid to generate a hydrogel [19–21,26,27]. So far, little is known about the structure of the chemically crosslinked MC hydrogels.

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Table 1
Water content of chemically cross-linked hydrogels of PVA, MC, and PVA/MC blend for various concentrations of glutaraldehyde. The concentration of HCl was 2.25×10^{-1} mol/l. The water content in hydrogel(W_c) was calculated using the expression $W_c = (W_s - W_d)/W_d$ where W_s is the weight of water saturated hydrogel, W_d is the weight of the dried hydrogel. The hydrogel was dried in a vacuum oven for 3 h at 100°C (sol.; soluble in water)

Concentration of glutaraldehyde (mol/l)	Water content in hydrogels (W_c)		
	PVA hydrogel	MC hydrogel	PVA/MC(20/80 wt/wt) blend hydrogel
0	Sol.	Sol.	Sol.
6.3×10^{-4}	0.59	Sol.	Sol.
2.5×10^{-3}	0.51	Sol.	Sol.
8.4×10^{-3}	0.49	0.56	0.55

There are detailed studies about the miscibility in blends of cellulose with PVA [4,8,9]. The PVA and MC, which are polyhydroxy compounds soluble in cold water, exhibit excellent miscibility in aqueous solutions but only partial miscibility in the solid state. PVA is a soft and elastic material, whereas MC is a more rigid and stiff one. We found that the blends of PVA with MC posses partial miscibility for low and intermediate MC contents and higher miscibility for high MC contents [35].

In the present paper, we prepared PVA/MC blend hydrogels by chemical crosslinking with glutaraldehide (GA) using HCl as catalyst, in an aqueous solution. The thermal and viscoelastic properties of blend hydrogels were investigated via differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

2. Experimental

2.1. Sample preparation

PVA(M_w 89,000–98,000, degree of deacetylation 99%), MC (M_n 17,000, degree of substitution (methoxy) 1.6–1.9) and glutaraldehyde (GA, 25 wt% solution in water) were purchased from Aldrich Chem. Co., and the water was double distilled. Aqueous polymer solutions (5 wt%) were first prepared by dissolving polymer powders in water and by heating at 80°C with stirring. GA and HCl were added after the polymer solution was cooled to room temperature. The blend film was prepared by casting the polymer solution on a glass plate and by drying for 72 h at the ambient temperature. The polymer solutions were glass filtered before casting in order to eliminate the insoluble impurities. The thicknesses of the obtained films were in the range of 50–80 μm.

2.2. Determination of the water absorbency of the hydrogels

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

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

where W_c is the water up-take per gram of hydrogel film, and W_s and W_d are the weights of the hydrogel films after swelling and subsequent drying, respectively. The time duration for swelling was 24 h. The excess water on the swollen films was wiped out with a filter paper.

2.3. Instrumentations

The DMA analysis was conducted using a DMA 2980 instrument (TA Instruments), in the tensile mode, at a frequency of 1 Hz, and by heating from −20 to 260°C at a rate of 2°C/min in a nitrogen atmosphere. The films with dimensions of about $3 \times 10 \times 0.1$ mm were subjected to sinusoidal deformation with a 5 μm amplitude. The DSC was performed with a DSC 2010 instrument (TA Instruments) in a nitrogen atmosphere. The thermal properties of the polymer blends were determined using two scans. The first heating scan, which was conducted to eliminate the residual water and solvent, was carried out at a rate of 20°C/min from room temperature up to 150°C and kept at the latter temperature for 5 min. The second scan was carried out at a heating rate of 10°C /min from 0 to 260°C. To determine the crystallization temperature, the samples were heated up to 250°C, kept at this temperature for 5 min and then cooled down at a rate of 20°C/min. The thermal decomposition was carried out with a TG/DTA 6200 instrument (Seiko Instruments Co., Japan), by heating from room temperature to 750°C at a heating rate of 20°C/min under a nitrogen flow. The mechanical properties of the polymer blends were determined with a Texture Analyser (Stable Micro System, UK). The tensile strengths and the elongations of the polymer blend films, which were conditioned in a 50% relative humidity atmosphere for 48 h, were determined at an extension rate of 500 mm/min, at room temperature.

3. Results and discussion

3.1. Swelling behavior

Water constitutes a suitable reaction medium, because PVA, MC and GA are soluble in water. The blend hydrogel was prepared by adding GA and HCl to the aqueous solution of the two polymers. The crosslinking took place through the reaction between the hydroxyl groups of the polyhydroxy polymers and the aldehyde groups of GA. The solutions of PVA and MC were optically clear over the entire weight ratio PVA/MC range. The solid films of the PVA hydrogels and MC hydrogels were highly transparent and clean. They became insoluble in water for sufficiently large degrees of cross-linking. The solid films obtained from solutions free of GA and HCl were transparent and homogeneous when the MC content was over 80 wt%, whereas

Table 2
Water content of chemically cross-linked hydrogels of PVA and MC for various concentrations of catalyst(HCl). The concentration of glutaraldehyde was 2.25×10^{-1} mol/l. The water content in hydrogel (W_c) was calculated as in Table 1 (sol.; soluble in water)

Concentration of HCl (mol/l)	Water content in hydrogels (W_c)		
	PVA hydrogel	MC hydrogel	PVA/MC(20/80 wt/wt) blend hydrogel
0	Sol.	Sol.	Sol.
7.0×10^{-3}	0.84	Sol.	Sol.
1.0×10^{-2}	0.79	0.81	0.81
2.8×10^{-2}	0.68	0.73	0.70
1.1×10^{-1}	0.51	0.58	0.56
2.3×10^{-1}	0.49	0.56	0.54

the solid blend hydrogel films became transparent for MC contents greater than 60 wt%. The swelling, expressed as gram of water up-take per gram of solid film, was used as a measure of the crosslinking density. The water up-takes of the hydrogels and the blend hydrogels are listed in Tables 1 and 2, respectively. Table 1 presents the effect of GA on the crosslinking density and Table 2 the effect of the catalyst (HCl) on the crosslinking density. The catalyst stimulates the acetalization between the hydroxyl groups of MC and the aldehyde groups of GA [26,27]. The MC hydrogels as well as the blend hydrogels became insoluble in water for HCl concentrations greater than 1.0×10^{-2} mol/l, while the PVA hydrogel became insoluble in water for HCl concentrations greater than 7.0×10^{-3} mol/l. As the crosslinking of PVA or MC increased, the number of hydroxyl groups of PVA and MC decreased and, as a result, the water-up-take decreased with increasing crosslinking density.

3.2. DSC analysis

The DSC thermograms of the PVA/MC blends are presented in Fig. 1 for various MC contents. PVA exhibited a relatively large and sharp endothermic curve, with a peak at 230°C, while MC, which is amorphous, had no endothermic curve. As the content of MC increased, the endothermic curve of PVA became broader and its peak shifted to lower temperatures. By blending PVA with an increasing amount of MC, the endothermic peak of PVA became less prominent and disappeared for 100 wt% MC. The depression of the melting temperature and the peak broadening indicate that the ordered association of the PVA molecules was decreased by the presence of MC. Fig. 2 presents the DSC thermogram of the chemically crosslinked PVA/MC blend hydrogels for various MC contents. The melting temperature of PVA hydrogel was 190.2°C, while the melting temperature of the pure PVA was 230°C. The melting temperature depression is caused by morphological and chemical modifications. The morphological changes involve the thickness of the crystallites and the degree of crystallinity. The chemical changes are results of the crosslinking and of the branching due to the grafting of the crosslinker [26]. Of course, the chemical changes affect the morphological ones. The endothermic peak decreased rapidly

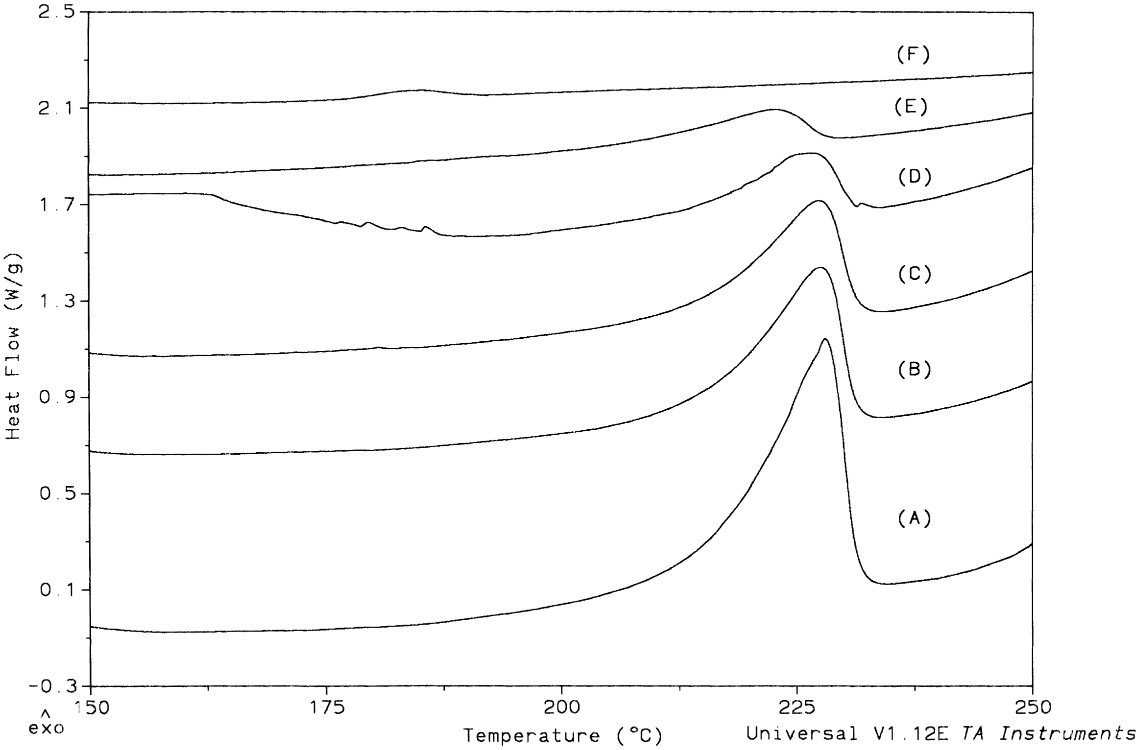

Fig. 1. DSC thermograms of PVA/MC blends for various MC contents. MC content(wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, and (F) 100. The measurement was conducted at a 10°C/min heating rate under nitrogen.

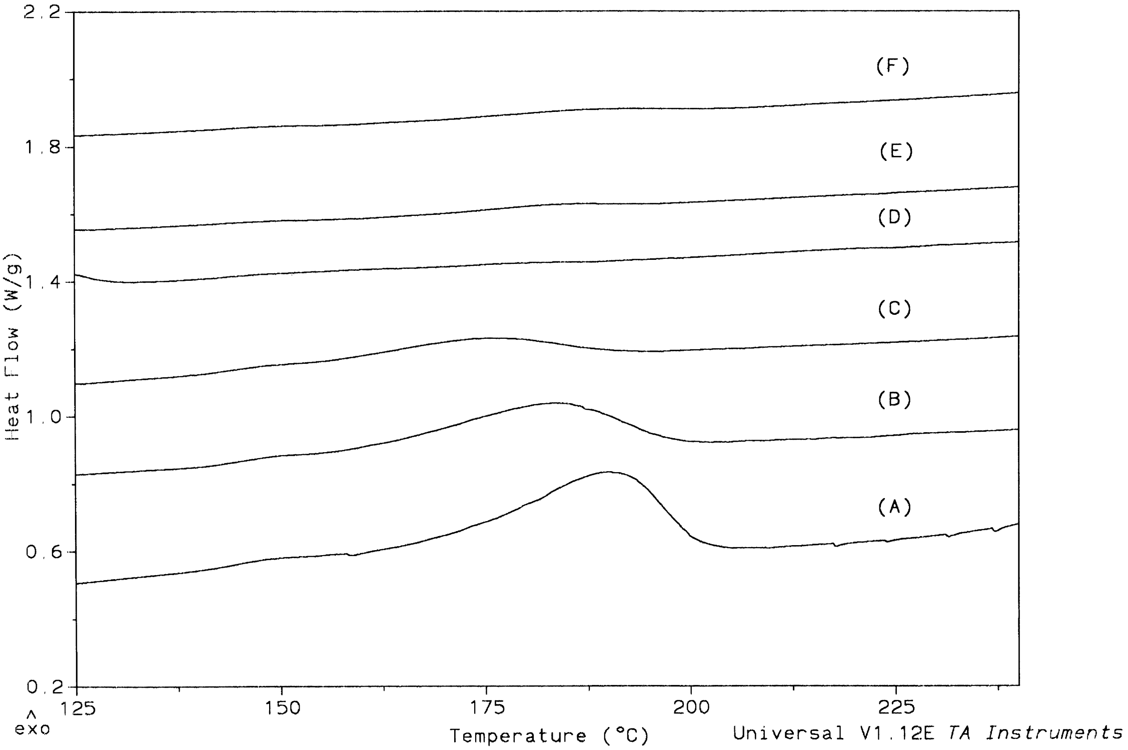

Fig. 2. DSC thermograms of PVA/MC blend hydrogels for various MC contents. MC content(wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, (F) 100. The concentration of GA and of HCl were 8.38×10^{-3} mol/l and 2.25×10^{-1} mol/l, respectively. The measurement was conducted at a 10°C/min heating rate under nitrogen.

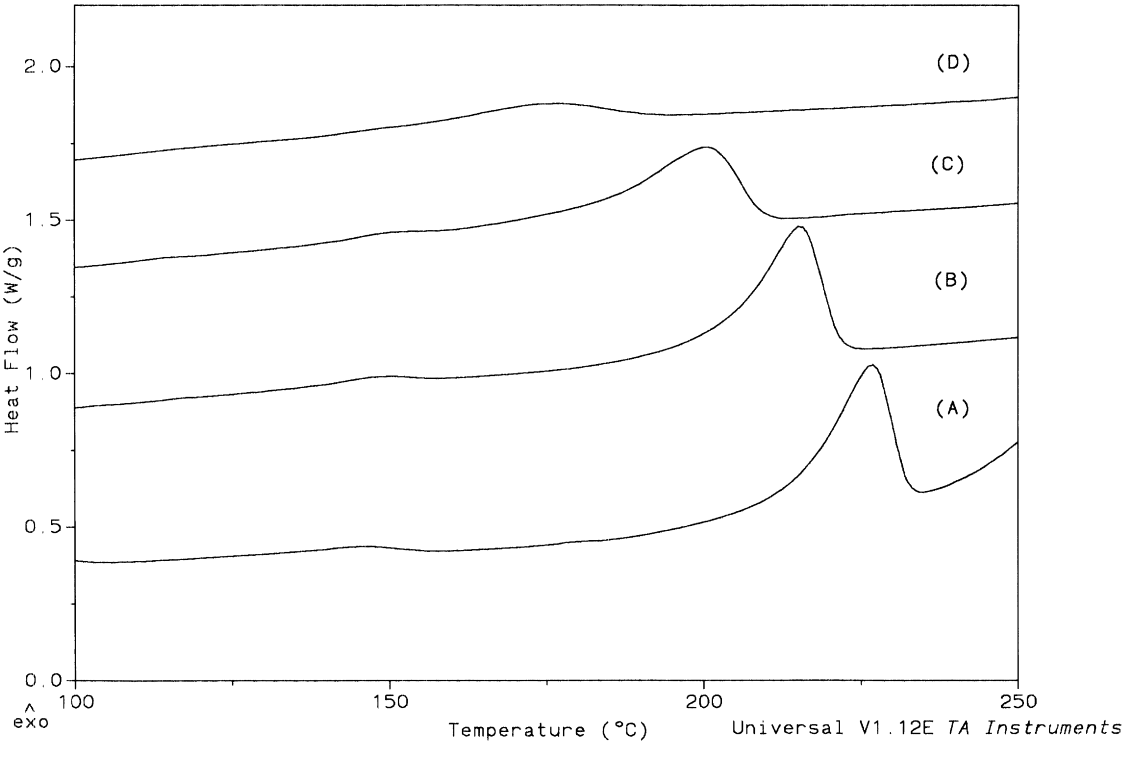

Fig. 3. DSC thermograms of PVA/MC blend hydrogels for various concentrations of glutaraldehyde: (A) 0 mol/l, (B) 6.25×10^{-4} mol/l, (C) 2.50×10^{-3} mol/l, (D) 8.38×10^{-3} mol/ml. The concentration of HCl was 2.25×10^{-1} mol/l. The blend wt ratio of PVA/MC was 60/40.

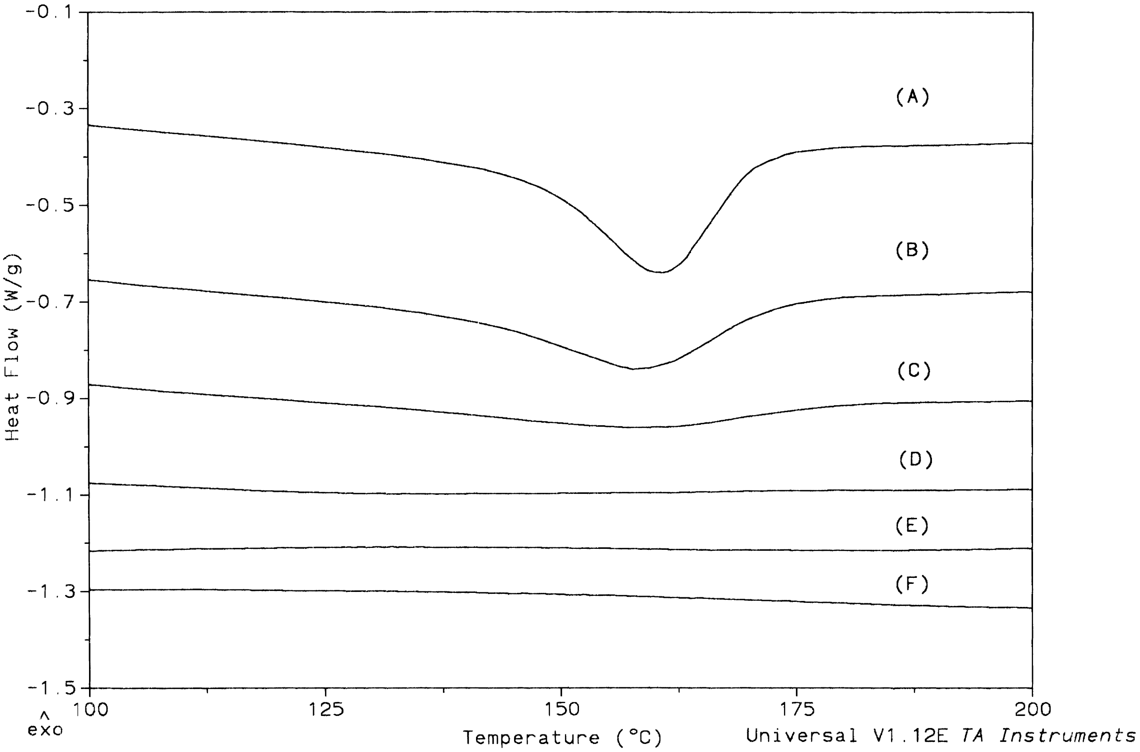

Fig. 4. DSC thermograms of PVA/MC blend hydrogels for various MC contents. MC content(wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, and (F) 100. The concentrations of GA and of HCl were 8.38×10^{-3} mol/l and 2.25×10^{-1} mol/l, respectively. The measurement was conducted at a −20°C/min cooling rate under nitrogen.

and disappeared for the samples containing over 60 wt% MC. The melting temperature depression and the peak broadening suggest that the PVA molecules are highly constrained by the entanglement of the two polymers due to the crosslinking of the blend with GA. Fig. 3 presents the DSC curves of blend hydrogels for a PVA/MC blend weight ratio of 60/40 and various GA concentrations. With increasing GA concentration, the endothermic peak shifted to the lower temperatures and became broader. A higher depression of the melting temperature and a larger peak broadening indicate that the ordered association of the PVA molecules was altered by both the presence of amorphous MC and chemical crosslinking of the PVA. For the PVA/MC(60/40, wt/wt) blend hydrogel, which was prepared with a GA concentration of 8.38×10^{-3} mol/l and HCl concentration of 2.25×10^{-1} mol/l, the endothermic peak almost disappeared, implying the absence of any crystalline domain in PVA. Fig. 4 presents the crystallization curves of the blend hydrogels obtained during a cooling process, and reveals that the exothermic peak of the crystallization temperature and the exothermic heat of crystallization decreased with increasing MC content and crosslinking density. The exothermic peak disappeared for MC contents greater than 40 wt%. These observations indicate that the ordered association of the PVA molecules is strongly constrained by the presence of the MC molecules and crosslinking.

3.3. DMA analysis

Fig. 5 presents the DMA thermograms of PVA, PVA hydrogel, MC, and MC hydrogel as mechanical loss tangent, tan δ, against temperature in the range of −20 to 260°C. The thermogram of the PVA film exhibits two peaks at 85 and 143°C, and a large peak above 210°C. The first peak at 85°C, designated as the α_a relaxation, represents the glass transition temperature of PVA. The relaxation observed at 143°C, designated as the β_c relaxation, is due to the relaxation in the PVA crystalline domains. The third relaxation, in the temperature range of 200–260°C, is caused by the melting of the crystalline domains of PVA. In contrast to the three relaxation peaks of PVA, the PVA hydrogels exhibit only two relaxation peaks, one below the α_a relaxation of PVA and the other above the β_c relaxation of PVA. The shifting of the α_a relaxation to the lower temperature indicates a decrease in the glass transition temperature of the PVA hydrogel compared to that of PVA free of crosslinking, which can be explained as follows. In PVA, the hydroxyl groups of PVA contribute, because of hydrogen bonding, to the stiffness of the linear polymer. When the number of hydroxyl groups decreases, by either branching, because of the grafting of the crosslinker, or crosslinking, the hydrogen bonding is attenuated and thus the chain stiffness, and hence the glass transition temperature is decreased. Fig. 5 also presents the temperature dependence

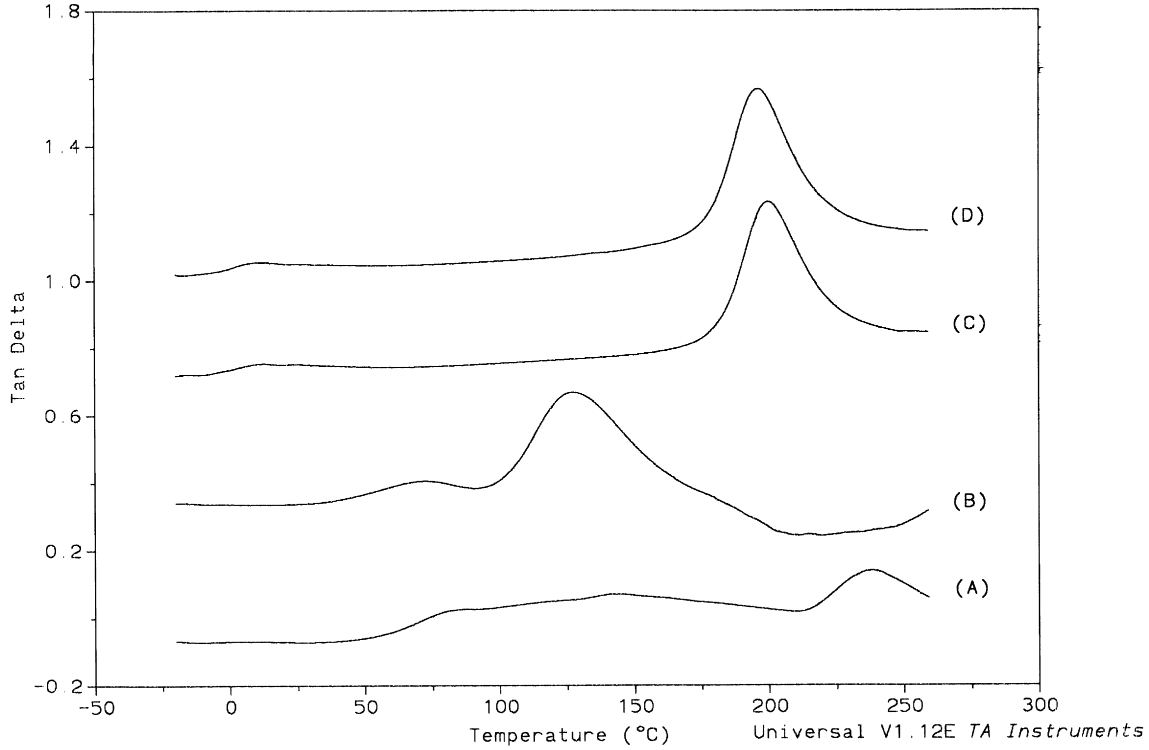

Fig. 5. Temperature dependence of tan δ for PVA (A), PVA hydrogels (B), MC (C), and MC hydrogel (D). PVA hydrogel and MC hydrogel were prepared with a GA concentration of 8.38×10^{-3} mol/l and HCl concentration of 2.25×10^{-1} mol/l. All films were vacuum dried at 100°C for 3 h prior to the DMA measurement.

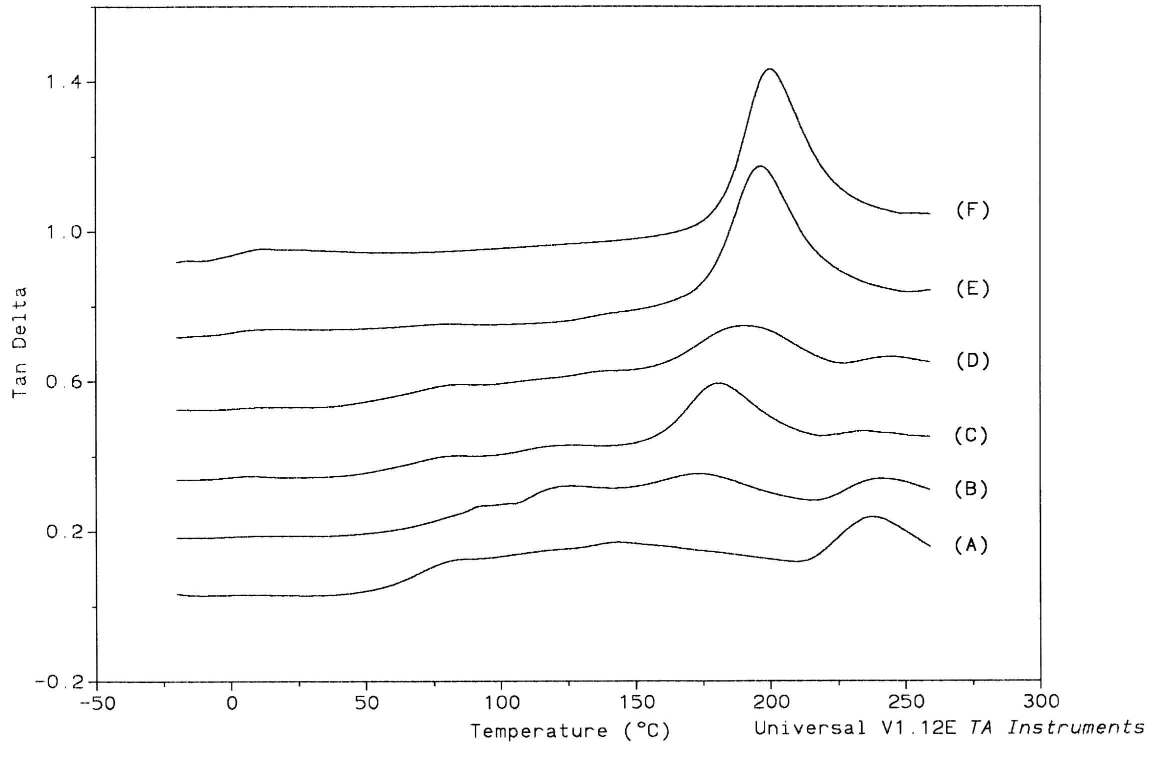

Fig. 6. Temperature dependence of tan δ for PVA/MC blends for various MC contents. MC content (wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, and (F) 100. All films were vacuum dried at 100°C for 3 h prior to the DMA measurement.

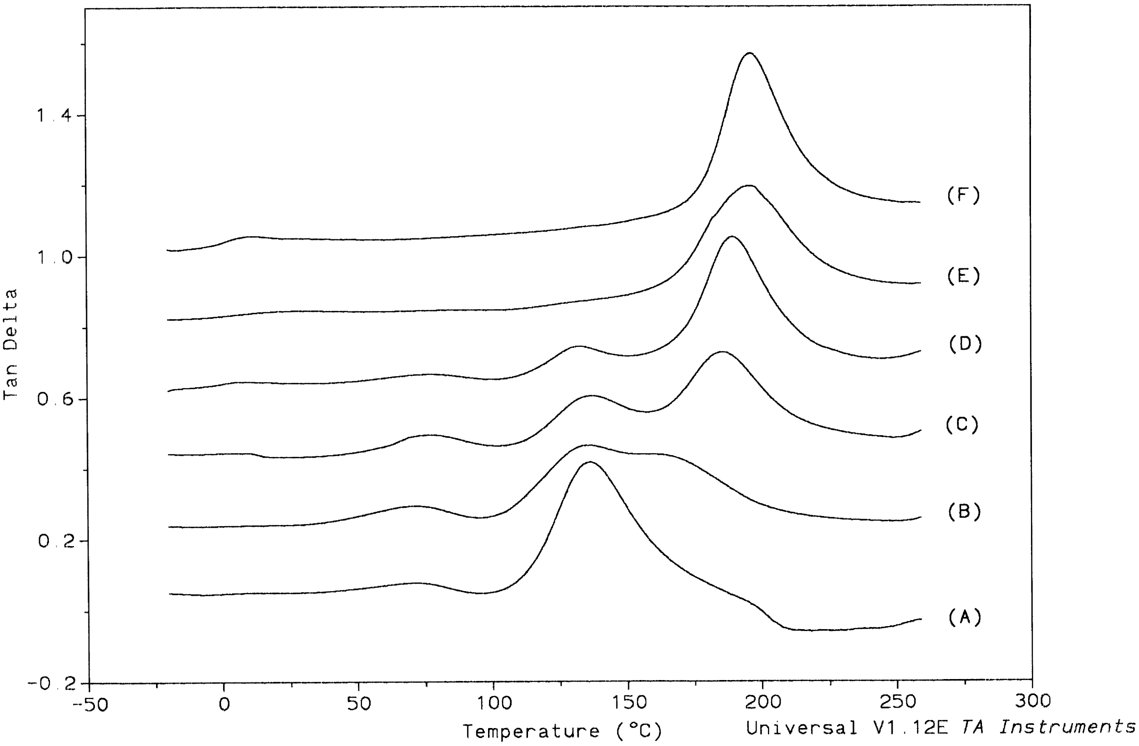

Fig. 7. Temperature dependence of tan δ for PVA/MC blend hydrogels for various MC contents. MC content(wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, and (F) 100. The GA concentration was 8.38×10^{-3} mol/l and HCl concentration 2.25×10^{-1} mol/l. All the films were vacuum dried at 100°C for 3 h prior to the DMA measurement.

of tan δ of an MC film in the temperature range of -20°C to 260°C. Two relaxation peaks, β and α can be observed at 26.8, and 200.8°C, respectively. The relaxation peak at 200.8°C corresponds to the glass transition temperature of MC. In contrast, for cellulose, no glass transition temperature could be detected before appreciable thermal degradation took place [4]. The tan δ curve for the MC hydrogel is very similar to that of MC, indicating that the rigidity of the MC backbone was not changed in a major way by crosslinking, even though the hydroxyl groups of the anhydroglucose units of MC reacted with the dialdehyde groups of GA and generated a three dimensional structure by inter- or intramolecular crosslinking.

Figs. 6 and 7 present the temperature dependence of

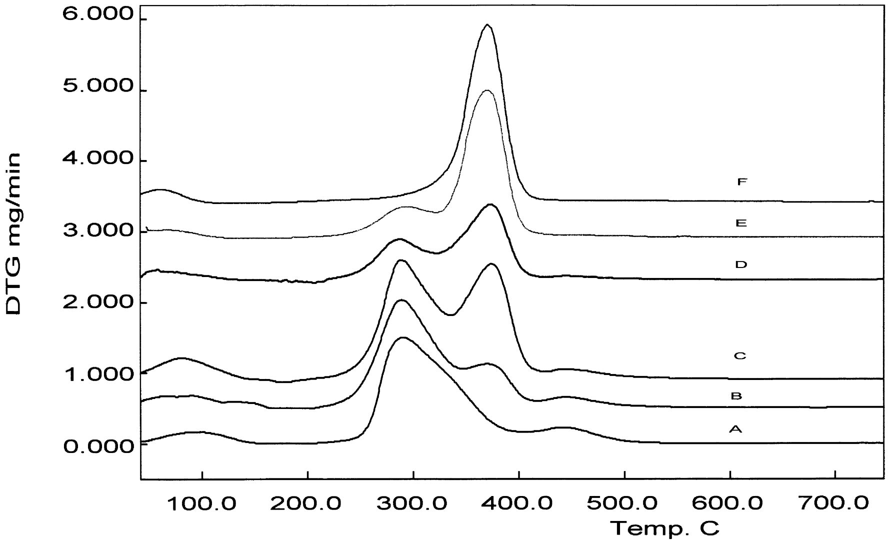

Fig. 8. Derivative of the thermogravimetric thermograms of PVA/MC blends for various MC contents. MC content(wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, and (F) 100. The measurement was conducted at a 20°C/min heating rate under nitrogen.

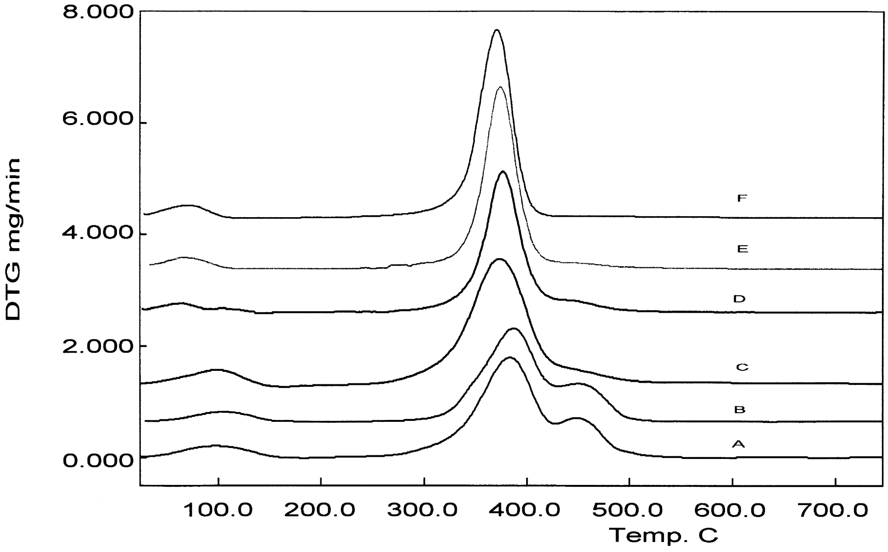

Fig. 9. Derivative of the thermogravimetric thermograms of PVA/MC hydrogels for various MC contents. MC content(wt%): (A) 0, (B) 20, (C) 40, (D) 60, (E) 80, and (F) 100. The concentrations of GA and of HCl were 8.38×10^{-3} mol/l and 2.25×10^{-1} mol/l, respectively. The measurement was conducted at a 20°C/min heating rate under nitrogen.

tan δ of PVA/MC blend and blend hydrogel films in the temperature range of −20°C to 260°C. Fig. 6 shows that the blends containing 20 wt% MC exhibit four relaxation peaks, three near to those of PVA and one near the α peak of MC. This means that the two components were only partially miscible. For an MC content of 40–60 wt%, the relaxation peaks of PVA became increasingly attenuated and the α peak of MC increasingly prominent. For MC contents over 80 wt%, a single peak remained, slightly displaced to a lower temperature when compared to the α relaxation of MC, implying complete miscibility between the two constituents. Visual observations indicated that the solid films of the blends were homogeneous and transparent when the MC content was higher than 80 wt%. Fig. 7 presents the temperature dependence of tan δ of PVA/MC blend hydrogels in the temperature range of −20 to 260°C and shows that the blend hydrogels containing more than 80 wt% MC have only one relaxation peak, implying a homogeneous miscible structure. The blend hydrogels with MC contents from 20–60 wt% exhibit three pronounced relaxation peaks, two for the PVA hydrogel and one for the MC hydrogel. Visual

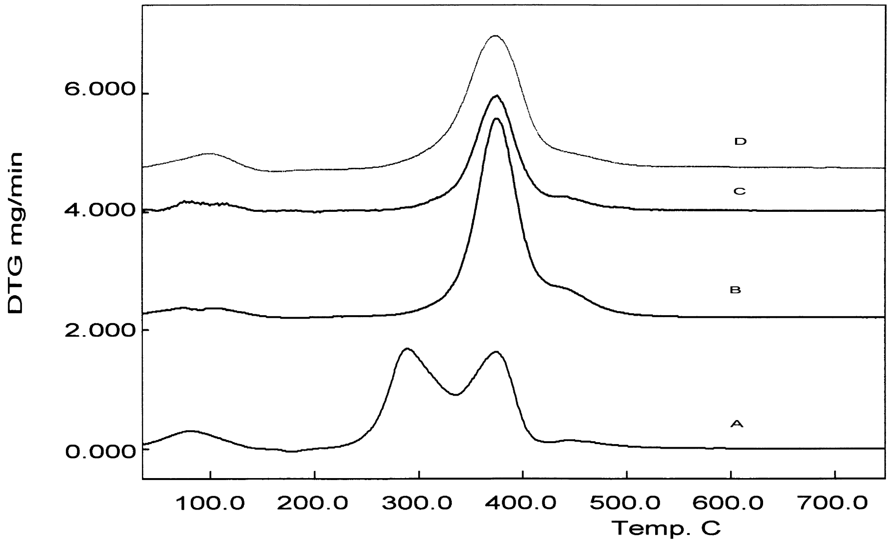

Fig. 10. Derivative of the thermogravimetric thermograms of PVA/MC blend hydrogels for various glutaraldehyde concentrations: (A) 0 mol/l, (B) 6.25×10^{-4} mol/l, (C) 2.50×10^{-3} mol/l, and (D) 8.38×10^{-3} mol/l. The concentration of HCl was 2.25×10^{-1} mol/l. Blend weight ratio of PVA/MC was 60/40. The measurement was conducted at a 20°C/min heating rate under nitrogen.

Table 3
Tensile strength and elongation of hydrogels of PVA and MC for various glutaraldehyde concentrations determined at an extension rate of 500 mm/min, at room temperature. The films were conditioned in a 50% relative humidity atmosphere for 48 h. The concentration of HCl was 2.3×10^{-1} mol/l

Concentration of glutaraldehyde (mol/l)	PVA		MC	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0	28.2	19.6	48.0	2.5
6.3×10^{-4}	30.8	18.9	49.2	2.3
2.5×10^{-3}	31.6	18.0	50.8	2.0
8.4×10^{-3}	33.3	14.0	52.1	1.4

observations indicated that, for the same MC content, the blend hydrogel films had higher homogeneity and transparency than the blend films.

3.4. TGA analysis

The TGA experiments with blends and blend hydrogels were carried out to find the effect of crosslinking on their thermal stability and thermal decomposition, and Fig. 8 presents the derivatives of the thermogravimetric (DTG) curves for blends with various MC contents. PVA exhibited one large peak followed by a small one (the latter above 400°C), while MC displayed a single large peak at a higher temperature than those of PVA. The blends exhibited two peaks, whose shapes and positions were dependent on composition. Fig. 9 presents the DTG curves of blend hydrogels. Figs. 8 and 9 show that the PVA hydrogel was more thermally stable than PVA and involved two degradation steps, while the MC and the MC hydrogels displayed a single peak at the same position, indicating that the crosslinking of MC did not affect its thermal stability. With the exception of the cases with MC contents below 20 wt%, the DTG curves of the blend hydrogels exhibited a single peak (Fig. 9), indicating a single degradation mechanism. Fig. 10 presents the effect of crosslinking on the blend hydrogels. The PVA/MC blend with 60/40 weight ratio had two peaks, while the blend hydrogels had a single peak. This suggests that there is a higher entanglement between the two components in the blend hydrogels.

Table 4
Tensile strength and elongation of hydrogels of PVA and MC for various concentrations of catalyst determined as in Table 3. The concentration of glutaraldehyde was 8.4×10^{-3} mol/l

Concentration of HCl (mol/l)	PVA		MC	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0	28.2	19.6	48.0	2.5
7.0×10^{-3}	29.0	19.0	50.9	2.3
1.0×10^{-2}	30.5	17.8	51.2	2.0
2.8×10^{-2}	31.5	16.9	52.0	1.5
1.1×10^{-1}	32.5	16.5	52.0	1.4
2.3×10^{-1}	33.3	14.0	52.1	1.4

3.5. Tensile strength/elongation measurements

The tensile strength and the elongation of the PVA hydrogels and MC hydrogels prepared with various GA and HCl concentrations are listed in Tables 3 and 4, respectively. From a structural point of view, PVA can be regarded as a flexible polymer, while MC as a more rigid one. The tensile strengths of PVA and MC hydrogels increased with increasing crosslinking density, whereas the elongation decreased. Table 5 lists the result obtained regarding the effect of the amount of MC on the mechanical properties of the blend hydrogels. For the blend hydrogels, the tensile strengths and elongations depend on the composition indicating that there is some miscibility between the two components [35].

4. Conclusions

PVA, MC and their blends were chemically crosslinked with glutaraldehyde in the presence of HCl as catalyst in an aqueous solution state. The degree of crosslinking of PVA and MC hydrogels, evaluated in terms of the amount of water up-take, increased with increasing concentrations of the crosslinker and catalyst. The DSC revealed that the PVA crystallinity in PVA hydrogel decreased drastically with increasing MC content and crosslinking. The depression of the melting temperature of PVA in the blend hydrogel was caused by the hydrogen bonding between the hydroxyl groups of the two polymers, which improved their miscibility. From the DMA experiments one could conclude that the PVA/MC blend hydrogel films exhibited partial miscibility up to 80 wt% MC and higher miscibility above 80 wt%. The TGA analysis showed that MC had a thermally more stable

Table 5
Tensile strength and elongation of blend hydrogels of PVA/MC for various contents of MC determined as in Table 3. The concentrations of glutaraldehyde and HCl were 8.38×10^{-3} mol/l and 2.25×10^{-1} mol/l, respectively

Content of MC in blend hydrogels MC (wt%)	Tensile strength (MPa)	Elongation (%)
0	33.4	14.0
20	30.1	6.5
40	26.5	4.0
60	35.5	4.2
80	42.5	3.9
100	52.1	1.4

structure than PVA and that its thermal stability were not changed by crosslinking, while the thermal stability of PVA was improved by crosslinking. The PVA/MC blends (60/40 wt/wt) exhibited two thermal degradation steps, while the blend hydrogels exhibited only one thermal degradation step. The DSC and TGA experiments indicated that the PVA and MC in the blend films displayed partial miscibility. The relatively good miscibility of the two polymers, each with abundant hydroxyl groups, over the entire composition range can be attributed to the hydrogen bonding. The miscibility of the blend can be improved by crosslinking the two polymers.

References

[1] Paul DR, Newman S. Polymer blends. New York: Academic, 1978.
[2] Olabisi O, Robinson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic, 1979.
[3] Nishio Y, Manley RStJ. Polymer 1987;28:1385.
[4] Nishio Y, Manley RStJ. Macromolecules 1988;21:1270.
[5] Cassu SN, Felisberti MI. Polymer 1997;38:3907.
[6] Tanaka T, Ohnishi S, Yamura K. Polym Int 1999;48:811.
[7] Wang Q, He L. Polymer 1997;38:3931.
[8] Kondo T, Sawatari C, Manley RStJ, Gray DG. Macromolecules 1994;27:210.
[9] Sawatari C, Kondo T. Macromolecules 1999;32:1949.
[10] Hong JH, Kim JY, Lee YM, Kim KY. J Appl Polym Sci 1992;45:1711.
[11] Iio K, Minoura N, Nagura M. Polymer 1995;36:2579.
[12] Miura K, Kimura N, Suzuki H, Miyashita Y, Nishio Y. Carbohydr Polym 1999;39:139.
[13] Monteir Jr. OAC, Airoldi C, Int. J Biol Macromol 1999;26:119.
[14] Martien FL. Encyclopedia of polymer science and engineering, Vol. 17. New York: Wiley, 1986. p. 167.
[15] Hodge RM, Edward GH, Simon GP. Polymer 1996;37:1371.
[16] Muhlebach A, Muller B, Pharisa C, Hofmann M, Seiferling B, Guerry D. J Polym Sci, Part A 1997;35:3603.
[17] Pines E, Rins W. Macromolecules 1973;6:888.
[18] Liu M, Cheng R, Quian R. J Polym Sci, Polym Phys Ed 1995;33:1731.
[19] Horkay F, Zrinyi M. Macromolecules 1982;15:1306.
[20] Tomita E, Ikeda Y. J Polym Sci, Part A 1997;35:3553.
[21] Gimenez V, Reina JA, Mantecon A, Cadiz V. Polymer 1999;40:2759.
[22] Shihayama M, Kurokawa H, Nomura S, Muthukumar M, Stein RS, Roy S. Polymer 1992;33:2883.
[23] Koike A, Nemoto N, Inoue T, Osaki K. Macromolecules 1995;28:2339.
[24] Wise ET, Weber SG. Macromolecules 1995;28:8321.
[25] Muhlebach A, Muller B, Pharisa C, Hofmann M, Seiferling B, Guerry D. J Polym Sci Part A 1997;35:3603.
[26] Yeom CK, Lee KH. J Membr Sci 1996;109:257.
[27] Kim KJ, Lee SB, Han NW. Polym J 1993;25:129.
[28] Matsuyama H, Teramoto M, Urano H. J Membr Sci 1997;126:151.
[29] BeMiller JN. Encyclopedia of polymer science and engineering, Vol. 7. New York: Wiley, 1986. p. 601.
[30] Hirrien M, Desbrieres J, Rinaudo M. Carbohydr Polym 1996;31:243.
[31] Sarkar N, Walker LC. Carbonhydr Polym 1995;27:177.
[32] Hirrien H, Chevillard C, Desbrieres J, Rinaudo M. Polymer 1998;39:6251.
[33] Desbrieres J, Hirrien M, Ross-Murphy SB. Polymer 2000;41:2451.
[34] Arisz PW, Kauw HJJ, Boon JJ. Carbohydr Res 1995;271:1.
[35] Park JS, Park JW, Ruckenstein E. J Appl Polym Sci 2000 (in press).