

# A Dynamic Mechanical and Thermal Analysis of Unplasticized and Plasticized Poly(vinyl alcohol)/Methylcellulose Blends

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**ABSTRACT:** The miscibility of poly(vinyl alcohol) (PVA)/methylcellulose (MC) blends was investigated over the entire composition range using the dynamic mechanical analyzer (DMA) and the differential scanning calorimeter (DSC). On the basis of the glass transition temperature, determined by DMA, one could conclude that the blends exhibited some miscibility below 80 wt % of MC and a good miscibility above 80 wt % of MC. The highest depressions of the melting and crystallization temperatures of the blends compared to those of PVA, determined via DSC analysis, were observed for MC contents greater than 80 wt %. The miscibility between PVA and MC can be attributed to the hydrogen bonds formed between the two components. The DMA studies showed that water is a good plasticizer for PVA and poly(ethylene glycol) 400 (PEG 400), a good plasticizer for MC. The inclusion of both water and PEG 400 in the blends revealed a synergistic plasticizing effect, which resulted in an increased miscibility between PVA and MC over a greater range of MC compositions (>60 wt %). The elongations of PVA, MC, and their blends were found to increase with the addition of PEG 400, but the tensile strengths to decrease. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1825–1834, 2001

**Key words:** poly(vinyl alcohol); methylcellulose; miscibility; plasticizer; dynamic mechanical analysis

## INTRODUCTION

Over the last decades the polymer blends of synthetic polymers with natural polymers have been intensively investigated because they are useful as biomedical and biochemical materials, and are biodegradable. Polymer blending is an important method for modifying or improving the physical

properties of polymeric materials, and hence for increasing the range of their applications.<sup>1,2</sup> Polymer blending of synthetic polymers with natural polymers including polysaccharides is of major importance since it provides a wider utilization of the abundant biomass.<sup>3–17</sup>

Polyvinyl alcohol (PVA) is a polyhydroxy polymer, which is useful in practical applications because of its easy preparation and biodegradability; it is obtained via the hydrolysis of poly(vinyl acetate), the acetate groups being replaced by hydroxyls.<sup>18</sup> PVA is a highly crystalline polymer,

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whose crystallinity can be attributed to the small hydroxyl groups, which allow the chains to adopt a planar zigzag conformation.<sup>19,20</sup> The excellent chemical resistance and physical properties of PVA with its high tensile strength and good oxygen-barrier properties under dry conditions led to their broad industrial use. The biodegradability and water solubility of PVA ensure its easy degradation and elimination after use. Cellulose, a highly hydrophilic polymer, has anhydroglucose as the basic repeating unit. The characteristics of cellulose, such as the rigidity of its backbone chain and its insolubility in most solvents, can be attributed to the three hydroxyl groups of the anhydroglucose unit of cellulose, which generate both inter- and intramolecular hydrogen bonds. In order to solubilize cellulose in a solvent, hydrophobic groups must be incorporated along the anhydroglucose backbone, which can break both its hydrogen bonding and crystallinity. Methyl cellulose (MC) contains methoxy groups in the place of some of the hydroxyl groups along the anhydroglucose units. The conversion of some of the hydroxyl groups of the backbone into methyl ether groups appreciably increases the water solubility of cellulose by eliminating the intermolecular interactions due to hydrogen bonding, thus reducing its ability to aggregate.<sup>21,22</sup> The polymer blends of PVA, poly(vinyl pyrrolidone), polyacrylonitrile (PAN), or polyester, as synthetic polymers, with cellulose, a biopolymer, have been extensively studied.<sup>4–17</sup> However, there is a limitation in the use of cellulose, because of its poor solubility in most solvents. Recently, numerous polymer blends of cellulose with synthetic polymers have been prepared by employing more special solvents. Polymer blends of cellulose with PAN or PVA were prepared from polymer solutions in *N,N*-dimethylformamide (DMF)–nitrogen dioxide (NO<sub>2</sub>), dimethylsulfoxide (DMSO)–paraformaldehyde (RF), and *N,N*-dimethylacetamide (DMAc)–lithium chloride (LiCl).<sup>4–6</sup> In the polymer blends of cellulose with PAN or PVA, there is miscibility at molecular level between their amorphous domains, for cellulose contents above 50 wt %.<sup>4,5</sup> The interactions in these blends, which are responsible for the miscibility, can be attributed to the hydrogen bonds between the hydroxyl groups of the anhydroglucose units of cellulose and the functional groups of the synthetic polymers. Kondo et al. reported that there is a regioselective hydrogen bonding between cellulose and some functional synthetic polymers.<sup>23–27</sup> Somewhat surprisingly, there have

been few detailed studies dealing with polymer blends involving the modified cellulose, MC, which in contrast to cellulose is a water-soluble, amorphous polymer, and PVA, a water-soluble and elastic crystalline polymer. PVA and MC can be easily prepared as bulk materials, films or fibers and have good mechanical properties and biocompatibilities.<sup>18–22</sup>

We report on the miscibility in polymer blends of PVA and MC prepared by an aqueous solution casting method. We investigated the miscibility of the two polyhydroxy polymers in the solid state by thermal and dynamic mechanical analyses. We also examined the effect of plasticizers (low molecular weight poly(ethylene glycol) in conjunction with water) on the miscibility, thermal properties, and mechanical properties of these polymer blends.

## EXPERIMENTAL

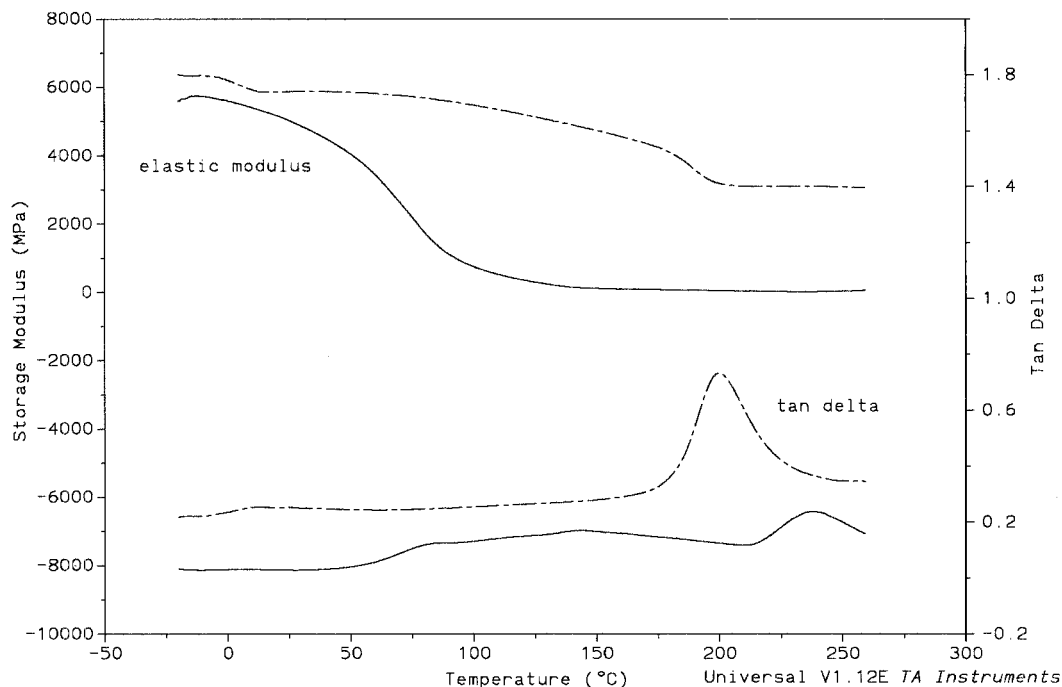
### Sample Preparation

PVA ( $M_w$  89,000–98,000, degree of deacetylation = 99%) and MC ( $M_n$  17,000) were purchased from Aldrich Chemical Co., Inc. Poly(ethylene glycol) (PEG 400) ( $M_w$  400) was supplied by Yakuri Pure Chem. (Japan). Water was double distilled. A known amount of PVA or MC was first dispersed in ethyl alcohol (5%) and then dissolved in water to prepare a 5 wt % solution at 80°C with stirring. The blend films were prepared by casting the mixed solutions on a glass plate. To eliminate the insoluble impurities, the polymer solutions were glass filtered before casting. The plasticizer was added to the polymer solution. The films were prepared by drying at room temperature for 48 h; film thicknesses of 50–80 μm were thus obtained.

### Measurements

The dynamic mechanical analysis (DMA) was conducted using a DMA 2980 instrument (TA Instruments) in the tensile mode at a frequency of 1 Hz by heating from –20 to 260°C, at a rate of 2°C/min, in a nitrogen atmosphere. The cast films, with dimensions of about 3 × 10 × 0.1 mm, were subjected to sinusoidal deformations with a 5 μm amplitude.

The differential scanning calorimetry (DSC) was conducted with a DSC 2010 instrument (TA Instruments) in a nitrogen atmosphere. The thermal properties of the homopolymers and polymer



**Figure 1** Temperature dependence of the storage modulus ( $E'$ ) and  $\tan \delta$  determined at  $2^\circ\text{C}/\text{min}$  scanning rate, 1 Hz frequency, and  $5 \mu\text{m}$  amplitude. PVA and MC were dried at  $100^\circ\text{C}$  for 3 h under vacuum. (—) PVA thermogram and (---) MC thermogram.

blends were analyzed by employing two scans. The first heating scan, carried out to eliminate the residues of water and solvent in the films, was performed at a rate of  $20^\circ\text{C}/\text{min}$  from room temperature up to  $150^\circ\text{C}$  and kept at this temperature for 5 min. The second scan was carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  from 0 to  $260^\circ\text{C}$ . To determine the crystallization temperature, the samples were heated up to  $250^\circ\text{C}$ , kept at this temperature for 5 min, and then cooled down at a rate of  $-20^\circ\text{C}/\text{min}$ .

The thermal decomposition measurements were conducted by employing a TG/DTA 6200 instrument (Seiko Instruments Co.) and by heating from room temperature to  $750^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  under a nitrogen flow.

The mechanical properties of the polymer blends were determined using a Texture Analyser (Stable Micro System, UK). The tensile strength and the elongation of the blend films, which were conditioned in a 50% relative humidity atmosphere for 48 h, were measured at an extension rate of  $500 \text{ mm}/\text{min}$ , at room temperature.

## RESULTS AND DISCUSSION

The aqueous polymer solutions of homopolymers of PVA and MC and their mixtures were optically

clear, and neither phase separation nor precipitation took place over the entire range of compositions, at room temperature, for 3 months. The solid films prepared from aqueous polymer solutions of the homopolymers were transparent and homogeneous, but those prepared from the aqueous solutions of polymer mixtures were dependent on the MC content. Above 80 wt % MC, the solid films of the PVA/MC blends were transparent and homogeneous, which indicated that no phase separation at a scale larger than about  $1 \mu\text{m}$  occurred. The films containing PEG 400 as a plasticizer were almost transparent and homogeneous for MC contents greater than 60 wt %.

The DMA thermograms of PVA and MC homopolymers in the dry state are presented in Figure 1, which provides the temperature dependence of the dynamic storage modulus ( $E'$ ) and the mechanical loss tangent ( $\tan \delta$ ). The PVA films exhibited two small peaks of  $\tan \delta$  at  $85^\circ\text{C}$  and  $143^\circ\text{C}$  and a large peak above  $210^\circ\text{C}$ . The peak at  $85^\circ\text{C}$  can be assigned to the  $\alpha_a$  relaxation corresponding to the glass transition temperature of PVA; there is a large decrease of  $E'$  around this temperature. The relaxation observed above  $100^\circ\text{C}$  ( $143^\circ\text{C}$ ), the  $\beta_c$  relaxation, is most likely caused by changes in the motions of the PVA chains.<sup>4,5</sup> The third transition in the  $220$ – $260^\circ\text{C}$

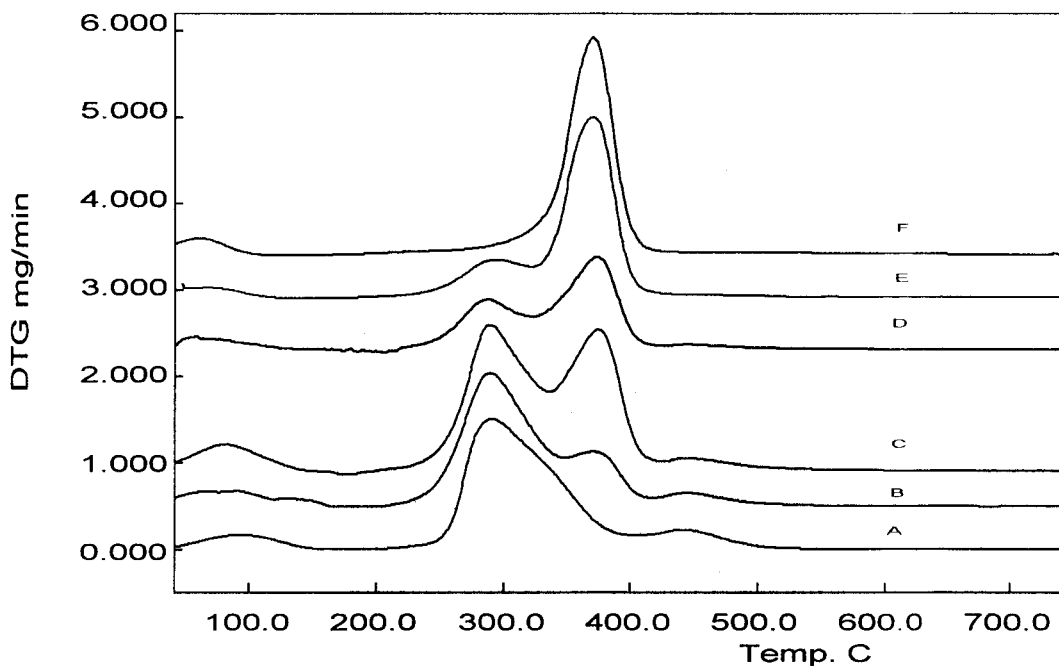
temperature range is caused by the melting point of the crystalline phase of PVA. (Takayanagi et al. reported that water cast PVA films exhibited as many as five mechanical relaxations.<sup>28</sup>) MC exhibited two  $\tan \delta$  peaks at 199 and 9°C. The large peak in  $\tan \delta$  curve at 199°C can be assigned to the  $\alpha$  relaxation, corresponding to the glass transition of MC, while the peak at 9°C is most likely caused by the local molecular motions of the MC main chains or the conformational changes of the MC side chains. The glass transition temperature of the unmodified cellulose cannot be detected by DMA, because it takes place in the 200–250°C range and appreciable thermal degradation begins to occur below this temperature range.<sup>4</sup> With the conversion of some of the hydroxyl groups of the anhydroglucose units into methyl ether groups, MC becomes water soluble and exhibits a lower glass transition temperature than cellulose. The high glass transition temperature and the insolubility in most solvents of the cellulose can be attributed to the three hydroxyl groups of the anhydroglucose units, which generate both intra- and intermolecular hydrogen bonds.

The thermal degradation behaviors of PVA and MC are presented in Figure 2, which shows that MC is more stable thermally than PVA. MC started to decompose thermally at 332°C (a

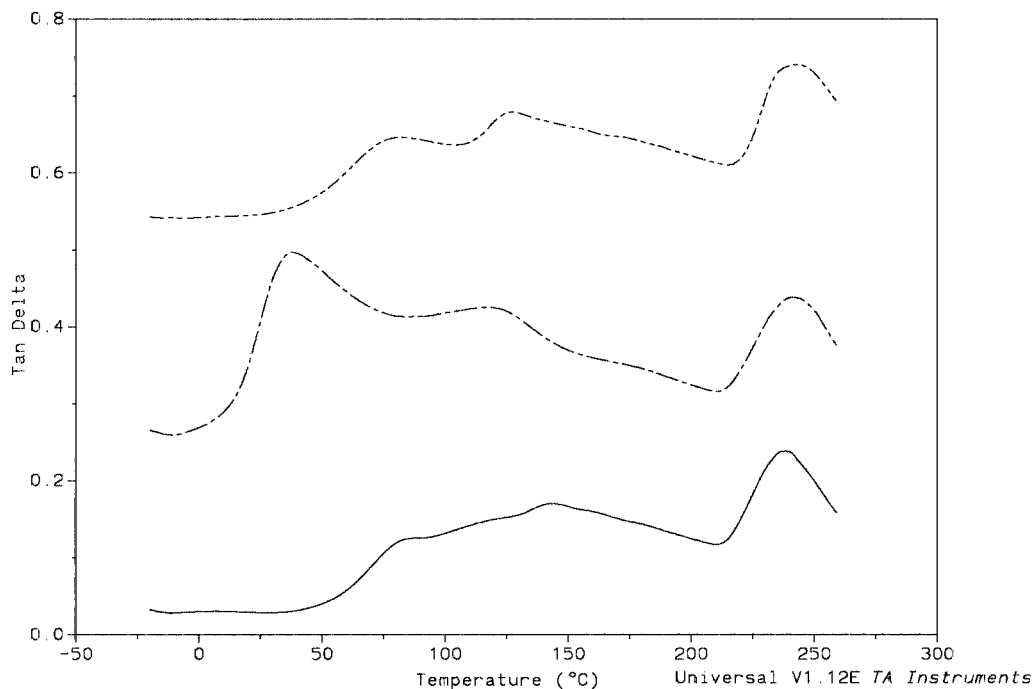
higher temperature than that for cellulose) and this allowed us to determine its glass transition temperature by DMA. Figure 2 shows that the thermal degradation of the blends of PVA with MC took place in one degradation step and is dependent on the composition of the blend.

The effect of water and of a low molecular weight plasticizer on the hydrophilic polymers was also investigated by DMA. Figure 3 presents the thermograms of PVA. For a PVA that contained around 5 wt % water, a first peak was observed at 38°C, the  $\alpha_a$  relaxation, and a second one at 118°C, the  $\beta_c$  relaxation. Compared to the dry PVA, whose glass transition temperature was 85.3°C, the figure indicates that the glass transition of PVA was significantly lowered by the plasticizing effect of water.<sup>19,20</sup> The inclusion of PEG 400 in PVA lowered much less the glass transition temperature of PVA (the  $\alpha_a$  relaxation) from 85.3 to 81.0°C.

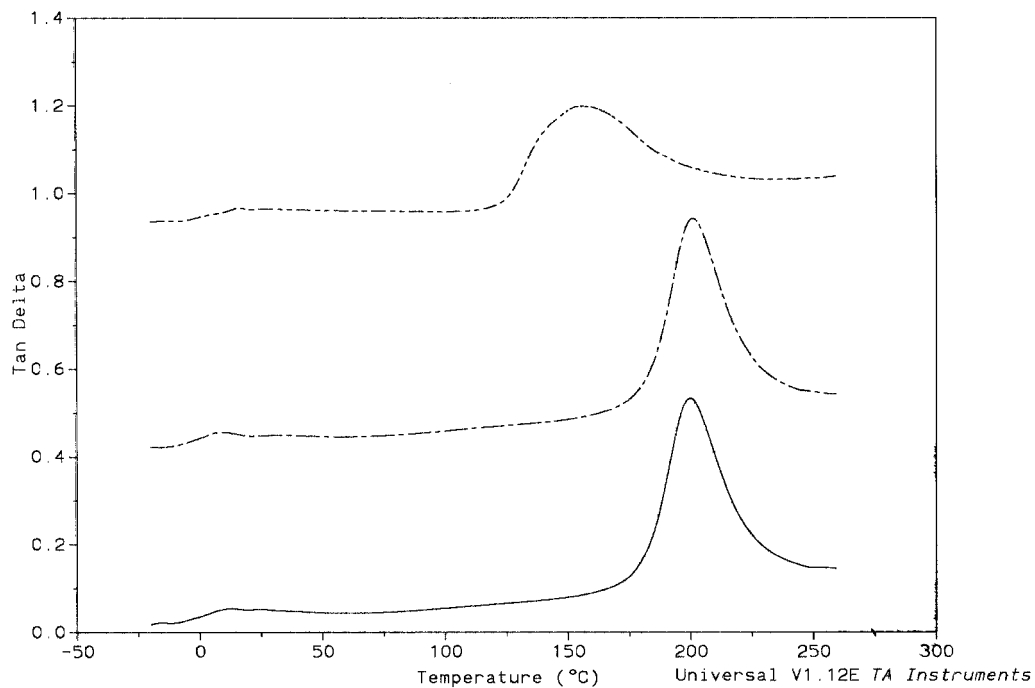
Figure 4 presents the DMA thermograms of MC and shows that PEG 400 was a good plasticizer since it lowered the glass transition temperature from 199.6 to 155.3°C. Water had no effect on the glass transition temperature of MC. Good miscibility with the plasticizer was observed in the plasticized PVA or MC containing up to 15 wt % of PEG 400.



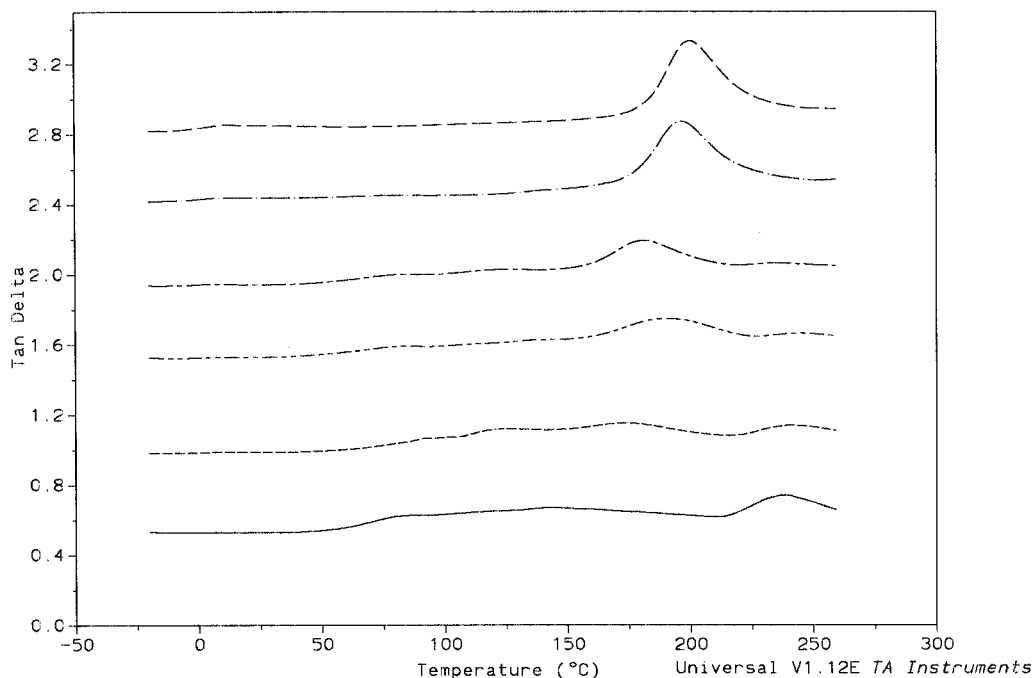
**Figure 2** TGA thermograms of PVA and MC determined at 20°C/min scanning rate for a series of samples with the weight ratios PVA/methylcellulose: (A) 100/0, (B) 80/20, (C) 60/40, (D) 40/60, (E) 20/80, and (F) 0/100.



**Figure 3** Temperature dependence of  $\tan \delta$  determined at 2°C/min scanning rate, 1 Hz frequency, and 5  $\mu\text{m}$  amplitude. PVA (—) was dried at 100°C for 3 h under vacuum. Hydrated PVA (---) containing 5 wt % water. PEG 400 plasticized PVA (- - -) containing 10 wt % PEG.



**Figure 4** Temperature dependence of  $\tan \delta$  determined at 2°C/min scanning rate, 1 Hz frequency, and 5  $\mu\text{m}$  amplitude. MC (—) was dried at 100°C for 3 h under vacuum. Hydrated MC (---) containing ca. 5 wt % water. PEG 400 plasticized MC (- - -) containing 10 wt % PEG.



**Figure 5** Temperature dependence of  $\tan \delta$  determined at  $2^\circ\text{C}/\text{min}$  scanning rate, 1 Hz frequency, and  $5 \mu\text{m}$  amplitude for various weight ratios PVA/methylcellulose: (—) 100/0, (- - -) 80/20, (- · -) 60/40, (- - -) 40/60, (- · ·) 20/80, and (- —) 0/100.

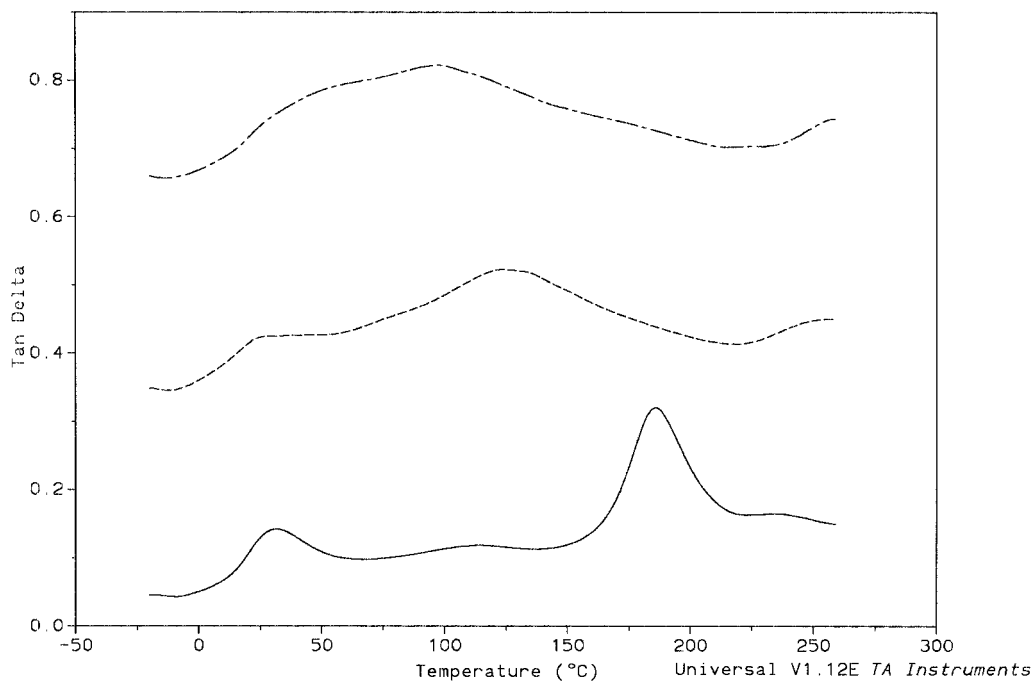
The DMA thermograms of the dry blends of PVA and MC are presented in Figure 5. They show that the position of the  $\alpha_a$  relaxation of PVA in  $\tan \delta$  curve has changed only slightly, but that the  $\beta_c$  relaxation peak became increasingly less prominent with increasing MC concentration. This observation indicates that the inclusion of MC influenced only little the relaxation of the PVA main chains, but that the crystallinity of PVA decreased with increasing MC content. The position of the  $\alpha$  relaxation of MC in the  $\tan \delta$  curve was shifted to lower temperatures and the peak breadth increased with increasing PVA content. This implies that the amorphous MC became partially miscible with PVA, particularly with the amorphous domains of PVA.<sup>4</sup> When the MC content increased over 80 wt %, the  $\tan \delta$  curves of the blends became very similar to those of MC. From this observation, it is reasonable to conclude that PVA and MC were partially miscible below 80 wt % MC, and that a higher miscibility, perhaps at the molecular level, occurred for blends containing more than 80 wt % MC.

The effect of water and PEG 400 on the blend miscibility was also investigated and Figure 6 presents the DMA thermograms for a blend of

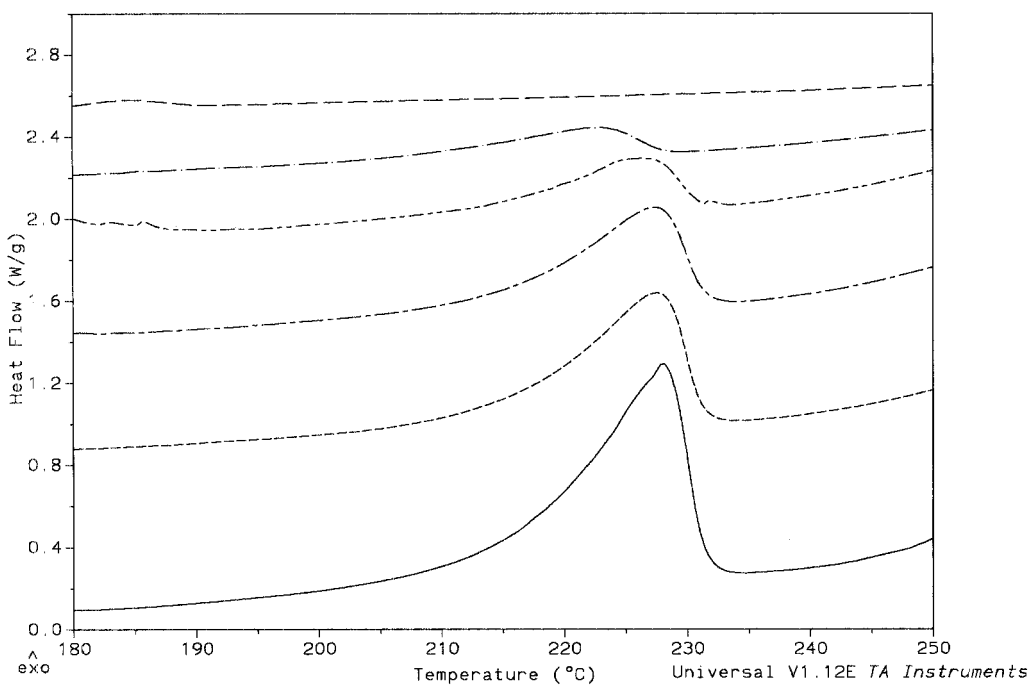
PVA with MC for a weight ratio of 60/40. The  $\tan \delta$  curve of the dried PVA/MC blends has two peaks for PVA, the  $\alpha_a$  and  $\beta_c$  relaxations, and two peaks for MC, the  $\alpha$  and  $\beta$  relaxations, indicating a relatively poor miscibility between the two polymers. However, Figure 6 shows that there are three peaks for the  $\tan \delta$  curve of the hydrated blends, one peak for PVA and two peaks for MC, indicating an improved miscibility between the two components. With the inclusion of PEG 400 in the blends, the temperature for the  $\alpha$  relaxation of MC decreases significantly, with an enlarged peak width. For the PVA/MC films containing both water and PEG 400, the  $\tan \delta$  curves exhibit one broad peak that combines the  $\alpha_a$  relaxation of PVA and the  $\alpha$  relaxation of MC. From these observations, it is reasonable to conclude that the new relaxation peak at  $124^\circ\text{C}$  represents the glass transition temperature of the polymer blend and that the miscibility of PVA and MC was improved by the synergistic effect of PEG 400 and water. Figure 6 shows that the storage modulus  $E'$  of the unplasticized blend is higher than those of the blends plasticized with water or both water and PEG 400.

The thermal properties of the homopolymers and their polymer blends were examined by DSC

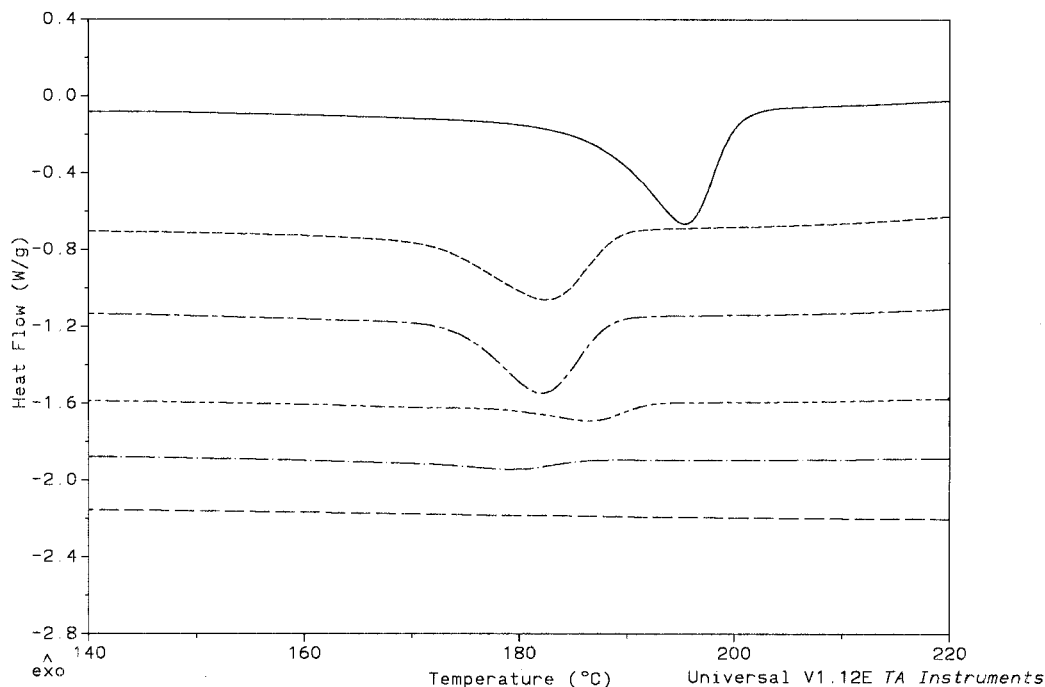




**Figure 6** Temperature dependence of  $\tan \delta$  determined at  $2^\circ\text{C}/\text{min}$  scanning rate, 1 Hz frequency and  $5 \mu\text{m}$  amplitude for blends of PVA/methylcellulose weight ratio of 60/40. Blend (—) was dried at  $100^\circ\text{C}$  for 3 h under vacuum. Hydrated blend (- - -) containing 5 wt % water. Hydrated blend (- · -) containing 10 wt % PEG 400 and 5 wt % water.



**Figure 7** DSC thermograms obtained for a  $10^\circ\text{C}/\text{min}$  second scanning rate for a series of samples with PVA/methylcellulose weight ratios of (—) 100/0, (- - -) 80/20, (- · -) 60/40, (- - -) 40/60, (- · ·) 20/80, and (- · -) 0/100.



**Figure 8** DSC thermograms obtained for a  $-20^{\circ}\text{C}/\text{min}$  scanning rate for a series of samples with PVA/methylcellulose weight ratio of (—) 100/0, (---) 80/20, (— —) 60/40, (— · —) 40/60, (· · ·) 20/80, and (— — —) 0/100.

and the results are given in Figures 7 and 8. Figure 7 presents the change of the thermal transition of PVA with the composition of the blend. No transition was exhibited by MC in the temperature range scanned. PVA exhibited a relatively large and sharp melting endotherm with a peak maximum at  $228.0^{\circ}\text{C}$ . By blending PVA with increasing amounts of MC, up to 80 wt %, the endothermic peak of PVA became increasingly less prominent and the melting temperature decreased. As shown in Table I, the heat of fusion, determined quantitatively by measuring the peak area, sharply decreased with increasing MC content; this indicates a decrease of the crystallinity of the PVA by its blending with the amorphous MC. Figure 8 presents the crystallization curves of the blends during cooling, and shows that the crystallization temperature and the exothermic heat of crystallization decreased with increasing MC content (Table I). The depressions of the melting temperature and heat of crystallization and the broadening of the peak indicate that the ordered association of the PVA molecules is restrained by the MC molecules, suggesting that the miscibility of the two components increases with increasing MC content. It is known that when one of the compo-

nents is crystalline, the depression of the melting point constitutes evidence for the miscibility of the pair.<sup>29</sup>

The data obtained from tensile strength and tensile elongation determinations for homopolymers and blends containing or free of PEG 400

**Table I** Heat of Fusion and of Crystallization of Homopolymers of PVA, MC, and Their Blends

Blend of PVA/MC, MC Content (wt %)	Heat of Fusion, $\Delta H_f$ (J/g) <sup>a</sup>	Heat of Crystallization, $\Delta H_c$ (J/g) <sup>b</sup>
0	59.5	33.9
20	36.2	23.7
40	26.3	21.9
60	12.7	4.1
80	7.1	2.4
100	0	0

<sup>a</sup> The first scan was run in an atmosphere of nitrogen at a heating rate of  $20^{\circ}\text{C}/\text{min}$  from room temperature to  $150^{\circ}\text{C}$ , where it stayed for 5 min. After rapid cooling to  $0^{\circ}\text{C}$ , the second scan was run in a nitrogen flow at a heating rate of  $10^{\circ}\text{C}$  up to  $260^{\circ}\text{C}$ .

<sup>b</sup> The sample was heated to  $250^{\circ}\text{C}$ , where it stayed for 5 min to eliminate residual and thermal stresses. Then it was cooled at a rate of  $-20^{\circ}\text{C}/\text{min}$  to room temperature.



**Table II Effect of MC Content and PEG 400 on the Tensile Strength and Tensile Elongation of Blends<sup>a</sup>**

Blend of PVA/MC, MC Content (wt %)	Tensile Strength (MPa)		Elongation (%)	
	PVA/MC	Plasticized PVA/MC	PVA/MC	Plasticized PVA/MC
0	25.3	21.8	16.3	23.7
20	19.8	19.3	5.9	9.0
40	30.3	18.4	3.6	1.6
60	27.3	15.8	1.2	1.7
80	37.1	29.1	2.7	4.1
100	44.6	36.4	2.5	4.6

<sup>a</sup> The content of PEG 400 in the blends was 10 wt %. The tensile strength and elongation of polymer blend films were determined at an extension rate of 500 mm/min at room temperature. Before testing, the samples were conditioned in a 50% relative humidity atmosphere for 48 h.

are listed in Table II. The tensile strength of PVA is higher than that of MC, whereas the elongation of PVA is lower than that of MC. With the inclusion of PEG 400, the tensile strengths of the homopolymers and polymer blends decrease, but the elongations increase.

## CONCLUSIONS

PVA/MC blend films could be easily prepared using an aqueous polymer solution casting method. The DMA results indicated high miscibility in the blends containing over 80 wt % MC. At compositions below 80 wt % MC, the blends exhibited only partial miscibility. The miscibility of the PVA/MC blends can be attributed to the hydrogen bonding between the hydroxyl groups of the two polymers. The depressions of the melting point and of the crystallization temperature of the blends compared to those of PVA, observed by DSC, support the above observation that there is miscibility in the blends due to specific interactions between the two components. The DMA indicated that water was an effective plasticizer for PVA and PEG 400 a good plasticizer for MC. A synergistic plasticizing action of PEG 400 and water on the polymer blends improved significantly the miscibility in the blends in a larger range of MC concentrations. The tensile strength decreased, while the elongation increased with the inclusion of PEG 400.

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