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Cellulose/Poly(vinyl alcohol) Blends Prepared from Solutions in *N*,*N*-Dimethylacetamide–Lithium Chloride

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ABSTRACT: Blend films of cellulose with poly(vinyl alcohol) (PVA) were prepared from mixed solutions in *N*,*N*-dimethylacetamide (DMAc)–lithium chloride (LiCl) by coagulation in a nonsolvent. The state of miscibility of the clear films obtained over the entire composition range was characterized by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and dynamic mechanical measurements. The WAXD and DSC results indicate that the crystallinity of PVA decreased drastically with increasing cellulose content and it exhibited no tendency to crystallize in the blends containing more than 70 wt % cellulose. The cellulose component showed a very low degree of crystallinity, even in the homopolymer film prepared in the same way. In a detailed estimation of the glass transition temperature by dynamic mechanical analysis, the coagulated blends were not totally miscible but showed a definite degree of partial miscibility in the composition range 0/100–60/40 of cellulose/PVA. Above 60 wt % cellulose content, however, it was found that there was considerable miscibility in the amorphous regions. The relatively good miscibility in this composition range may be due to the increased capability of the two polymers, each with abundant hydroxyl groups, to interact mutually through hydrogen bonding. The presence of such an interaction was supported by a melting point depression of PVA observed in the DSC characterization of the blends. Systematic depressions were also noted more markedly in the melting and crystallization temperatures in the DSC experiment carried out on the blends once melt recrystallized. This suggests that thermodynamic interaction between the two polymers is enhanced above the melting point of PVA, although the possibility of the presence of some kind of morphological effect is admitted.

Introduction

The importance of polymeric blends is now well established,[1,2] and both practical and fundamental studies have been conducted with a number of pairs of polymers. However, blends containing unmodified cellulose as one component have received relatively little attention,[3–6] except for mechanical blends in the form of fibers. One of the main reasons is that it has been difficult to prepare cellulose blends, owing to the poor solubility of the polymer in most organic solvents.

Quite recently we demonstrated that blend films of cellulose with polyacrylonitrile (PAN) could be easily obtained over the whole composition range from solutions in *N*,*N*-dimethylacetamide (DMAc)–lithium chloride (LiCl) by coagulation in a nonsolvent.[7] Furthermore, we showed from DSC and dynamic mechanical measurements that the cellulose/PAN blends exhibited considerable miscibility in the amorphous regions above 50 wt % cellulose content. The importance of the solvent DMAc–LiCl, in which no appreciable degradation of cellulose molecules occurs, has also been described in several papers[8–13] in relation to future practical developments of cellosics.

From a subsequent examination of the solubility of various conventional polymers in DMAc containing a certain amount of LiCl (usually 4–5 wt %), it was found that several important polymers including other vinyl polymers, polyamides (e.g., nylon 6), and polyesters (e.g., poly(ϵ-caprolactone)) could be blended with cellulose in a similar manner. Detailed studies of the blends of nylon 6 and poly(ϵ-caprolactone) with cellulose will be described elsewhere in the near future.[14] The purpose of the present paper is to report the preparation of cellulose/poly(vinyl alcohol) blends by using DMAc–LiCl and the miscibility characterization mainly through thermal analysis and dynamic mechanical testing. Both polymers are capable of forming strong, intra- and intermolecular hydrogen bonds between hydroxyl groups. Therefore, for the present system, it is also of interest to ascertain whether molecular interaction based on hydrogen bonding takes place between the two different polymers, contributing to enhancement of the state of miscibility in the blends.

Experimental Section

Materials. The cellulose sample used was a wood pulp with a degree of polymerization of 935. The other polymer, atactic poly(vinyl alcohol) (PVA), was purchased from Polysciences, Inc.; the nominal molecular weight was 78 000 and the saponification value was 99.7 mol %. Reagent-grade *N*,*N*-dimethylacetamide (DMAc) (Aldrich Chemical Co., Inc.) was stored for more than 1 week over potassium hydroxide before use. Lithium chloride (LiCl) (Aldrich Chemical Co., Inc.) was dried at 100–105 °C overnight and stored in a desiccator until used.

Preparation of Samples. A common solvent for both polymers, DMAc–LiCl, was used at a salt concentration of 4.5 wt %. A cellulose solution in DMAc–LiCl was prepared in almost the same way as applied in the previous study:[7] A wood pulp treated by a solvent-exchange technique[13] successively with water, methanol, and DMAc was added to DMAc–LiCl and the mixture was stirred at room temperature until dissolution of the cellulose fibers was almost complete. After continuous stirring for about 4 weeks, the resulting viscous solution was filtered through a coarse fritted-glass funnel under full mechanical pump vacuum. The actual concentration of cellulose in the solution was 1.4 wt %, as determined by weighing the solid film obtained from a portion of the solution by a coagulation method described below.

The original PVA sample supplied in powder form was immersed into acetone overnight to remove moisture, filtered, and dried under reduced pressure, before preparation of the solution in DMAc–LiCl. The PVA powder hardly dissolved in DMAc–LiCl at temperatures below ca. 60 °C. Above this temperature, however, the rate of dissolution of PVA increased remarkably. A 1.5 wt % PVA solution in DMAc–LiCl was prepared by dissolving the polymer at 70 °C under continuous stirring over a period of 2.5 h. The solution cooled to room temperature, in which no precipitate was observed, was filtered and stored in a closed container until used.

The two solutions thus separately prepared were mixed at room temperature in the desired proportions, so that the relative composition of the two polymers in the mixed solutions ranged from 10/90 to 90/10 in a ratio of weight percent, the first numeral referring to cellulose content throughout this work. After stirring for at least 2 days, the mixed solutions were used to prepare blend films by coagulation with ethanol. Each blend solution was poured into a rectangular Teflon tray with a flat bottom and then an

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appropriate amount of ethanol was carefully applied on the spread solution, whereupon cellulose/PVA blends were precipitated as a gelatinous film. The blends were steeped for about 1 h in ethanol and washed in several changes of methanol to thoroughly extract DMAc and LiCl. Following that, the gel films were again steeped in ethanol overnight and finally allowed to dry gradually at room temperature. An additional 24 h of drying at 50 °C under high vacuum was carried out on the solid films, before they were stored in a desiccator until used. Cellulose and PVA homopolymer films were also obtained by the same method as described above.

Measurements. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a flat-film camera using nickel-filtered Cu Kα radiation produced by a Philips X-ray generator.

Differential scanning calorimetry (DSC) was performed on ca. 15-mg samples with a Perkin-Elmer DSC-2C in an atmosphere of nitrogen. The instrument was calibrated with an indium standard. The thermal properties of the blends and homopolymers were usually analyzed in three scans: namely, the first heating, second heating, and cooling scans. The first heating scan was carried out for characterizing solution-coagulated films at a rate of 20 °C/min from 35 °C up to ca. 15 °C above the melting temperature (~230 °C) of plain PVA. In this scan, however, the thermograms were disturbed in the range of ca. 65–155 °C due to the presence of trace amounts of DMAc and/or water, and possibly due to other unknown effects (e.g., sintering of samples). Thus only the melting behavior will be reported as the DSC result for the as-coagulated samples. The second scan was done between the same limits of temperature after quick cooling (~200 °C/min) following the first heating, for characterizing the samples melt-crystallized in the DSC pan. An additional heating cycle was sometimes carried out and the response of the DSC traces was essentially reproducible after the first heating scan. The samples heated up to 242 °C were kept at this temperature for 5 min and then cooled at a rate of 20 °C/min to obtain the crystallization temperature. The calorimetric melting temperature, T_m, and the apparent enthalpy of fusion, ΔH_f, of each sample were determined from the maximum and the area of the melting peak, respectively. In similar manner, the crystallization temperature T_c and heat of crystallization ΔH_c were also evaluated from the exothermic curve peak in the cooling cycle. The glass transition temperature T_g, estimated in the second heating cycle, was taken as the temperature corresponding to 50% of the transition, i.e., the midpoint of the discontinuity in heat flow.

The dynamic storage modulus E', loss modulus E'', and mechanical loss tangent tan δ were measured with a Rheovibron Model DDV-II viscoelastometer (Toyo Baldwin Co., Ltd.) at 11 Hz in a nitrogen atmosphere. The temperature was raised at a rate of 1.2 ± 0.2 °C/min in the range −60 to 220 °C. For the dynamic tests, strips 2.5 × 30 mm cut from the best portion of the solution-coagulated films were employed. Prior to the measurement, the samples were sandwiched between a glass plate and a cardboard strip and heated in an oven at about 160 °C for 10 min, for complete removal of the last traces of solvents and moisture and relaxation of possible stresses.

Results and Discussion

Visual Observations. Not only the homopolymer solutions but also all the blend solutions of cellulose and PVA in DMAc–LiCl were optically clear to the naked eye. Even after the solutions were allowed to stand for more than 4 months at room temperature, they showed neither separation into bilayers nor any precipitation. It is interesting to note that the solubility of PVA in pure DMAc was inferior to that in the case where DMAc containing LiCl was used as the solvent. The dissolution of the original PVA powder in pure DMAc was incomplete until the temperature was raised to 90 °C. Furthermore, when the hot solution was cooled to room temperature, it formed a transparent gel. As has already been suggested by several workers,[9,11-13] cellulose is able to dissolve by forming some kind of complex with the solvent system DMAc–LiCl. For example, McCormick et al.[12,13] proposed that the hydroxyl protons on the anhydroglucose units hydrogen bond to the chloride anion Cl^- which is in turn associated with a Li-$[DMAc]^+$ macrocation. It is possible that a similar complexation may take place in the PVA solution in DMAc–LiCl, judging from the observation described above. Although the dissolution mechanism of PVA in DMAc–LiCl was not further examined in the present work, it is evident that the addition of LiCl to DMAc contributes at least to remarkably weakening the strong tendency for self-association of PVA caused by the interchain hydrogen bonding.

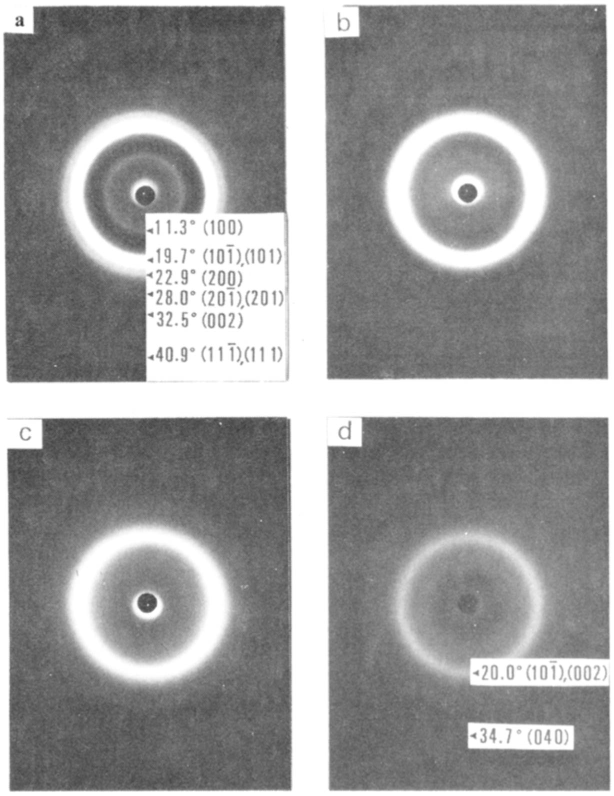

Figure 1. Wide-angle X-ray diffraction patterns for films of (a) PVA, (b) 50/50 cellulose/PVA, (c) 73/30 cellulose/PVA, and (d) cellulose, prepared from solutions in DMAc–LiCl.

Cellulose/PVA solid films obtained via a gelatinous state from the solutions by coagulation in ethanol were also optically clear irrespective of the blend composition. The blends containing more than 70 wt % PVA and the PVA homopolymer sample were heavily turbid in the swollen gel state immediately after precipitation; however, even these samples became transparent on drying. Under the optical microscope all the samples gave a dark, uniformly isotropic image between crossed polars, and no phase separation at any higher level above micron size could be perceived.

WAXD Characterization. The wide-angle X-ray diffraction (WAXD) patterns of selected coagulated samples are shown in Figure 1. The WAXD pattern of a pure PVA film (Figure 1a) is composed of several diffraction rings which could be indexed by using the lattice parameters a = 7.81, b = 2.52, and c = 5.51 Å and β = 91.7°, corresponding to the monoclinic unit cell given by Bunn.[15] The 2θ value and index (hkl) are denoted for the major Debye rings appearing in the pattern. On the other hand, the cellulose WAXD pattern, shown in Figure 1d, exhibited a diffraction profile based on the cellulose II modification, e.g., characterized by a diffraction ring at 2θ = 20.0° resulting from the (10$\bar{1}$) and (002) reflections and that at 2θ = 34.7° arising from the (040) reflection. Here it should be noted that the cellulose diffraction rings are considerably diffuse, indicating a low degree of crystallinity. This is in large part due to the mild precipitation conditions used in the preparation of the sample; i.e., as was stated

Table I
Melting Temperature T_m, Crystallization Temperature T_c, Glass Transition Temperature T_g, Heat of Fusion ΔH_f, and Heat of Crystallization ΔH_c of Cellulose/PVA Blends, Measured by DSC

cellulose/PVA, w/w	1st heating		2nd heating		cooling		
	T_m, °C	ΔH_f, cal/g	T_g, °C	T_m, °C	ΔH_f, cal/g	T_c, °C	$-\Delta H_c$, cal/g
0/100	229.8	24.2	80	230.1	18.7	195.9	17.5
10/90	227.2	19.2 (21.3)[d]	82	226.8	14.7 (16.3)[d]	191.5	12.7 (14.1)[d]
20/80	226.6	16.1 (20.1)	83	224.5	12.4 (15.5)	182.8	10.9 (13.6)
30/70	223.5	11.4 (16.2)	85	220.3	9.4 (13.4)	174.1	7.7 (11.0)
40/60	222.5	7.6 (12.6)	87	212.9	6.2 (10.3)	164.3	4.6 (7.7)
50/50	217.7	4.8 (9.6)	90	205.6	4.0 (8.0)	158.4	2.6 (5.2)
60/40	211.5	3.0 (7.5)	~90[e]	197.0	2.0 (5.0)	143.7	NE
70/30	NE[b]	NE	ND	~189[e]	NE	NE	~0
80/20	NE	~0	ND	NE	~0	ND	
90/10	ND[c]		ND	ND		ND	
100/0	ND		ND	ND		ND	
70/30[a]	229.3	6.9 (23.0)	83	226.5	5.3 (17.7)	not tested	
80/20[a]	229.5	3.8 (19.0)	80	228.0	3.1 (15.5)	not tested	

[a] Mechanical mixture of both polymers as a fine powder. [b] NE = could not be estimated. [c] ND = not detected. [d] Based on weight of PVA. [e] Estimated with great uncertainty.

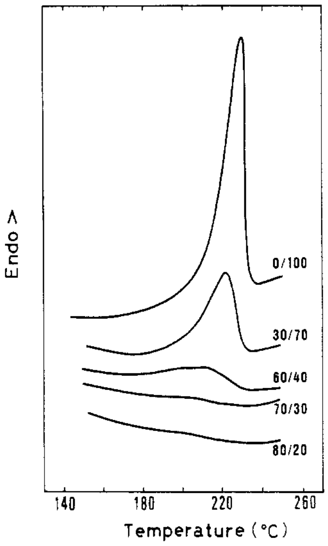

Figure 2. DSC melting thermograms in the first heating cycle carried out for selected cellulose/PVA blends regenerated from solutions in DMAc–LiCl.

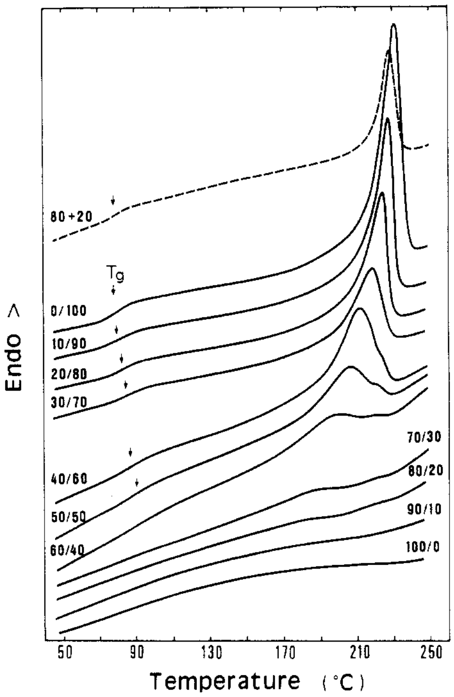

Figure 3. DSC thermograms in the second heating cycle for a series of cellulse/PVA blends. The broken-line curve is a thermogram obtained for a mechanical blend (80 + 20) of fine pwoders of both polymers. The sensitivity of the scans for the samples containing more than 40 wt % cellulose is twice that for the others.

previously,[7] celluloses regenerated in nonaqueous media with avoidance of stress are predominantly amorphous.[16] In the WAXD patterns of the blends, there was no definitive evidence of the formation of a so-called mixed-crystal structure. However, it was qualitatively observed that the crystallinity of each polymer was strongly affected by the presence of the other component, i.e., the diffraction intensities of the individual polymers decreased drastically with increasing content of the other component. For example, the WAXD intensities of the PVA component were seriously reduced as cellulose was blended up to 40 wt %, and in a 50/50 blend the PVA diffraction rings at 2θ = 28.0° and 32.5° were no longer detectable and the (100) and (200) reflections were observed with vanishingly small intensity in the WAXD pattern, as illustrated in Figure 1b. When the cellulose content reached 70 wt %, the diffraction profile of the PVA crystals was hardly discernible as can be seen from the WAXD pattern given in Figure 1c. Similarly the blends containing more than 70 wt % PVA gave WAXD patterns where no appreciable diffraction maximum of cellulose crystals could be perceived.

DSC Characterization. Thermal properties of the cellulose/PVA blends were examined by differential scanning calorimetry (DSC). It was of particular interest to estimate how the thermal transitions of PVA varied with the composition of the blends, since the cellulose homopolymer films prepared in this work showed no significant transition in the temperature range of the DSC scan. The results of the measurements are shown in Figures 2–4, and thermodynamic values obtained through analysis of the DSC curves are summarized in Table I.

(a) As-Coagulated Samples (First Heating). Figure 2 displays several examples of the melting thermograms obtained in the first heating scan carried out on the solution-coagulated films. The pure PVA sample gives a relatively large and sharp melting endotherm with a peak maximum (T_m) at around 230 °C. As cellulose is blended with PVA up to 60 wt %, the endothermic peak of PVA tends to lose its prominence with accompanying depression in the T_m values. In the blends containing 30 wt % or less PVA, it becomes difficult to clearly detect the melting endotherm in the DSC curves. The magnitude of the endotherms can be assessed more quantitatively by measuring the peak area. Values of the heat of fusion per

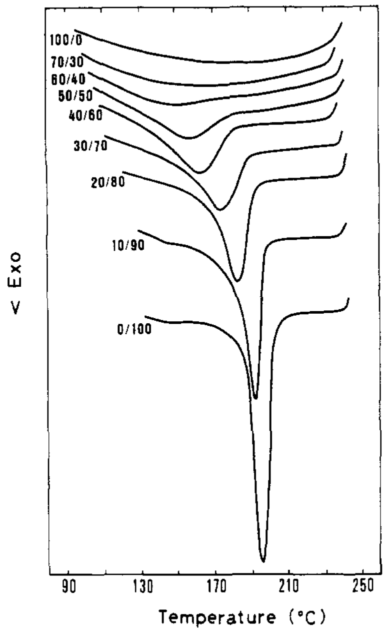

Figure 4. DSC thermograms for crystallization of PVA in blends with cellulose, obtained in the cooling process. The sensitivity of the scans for the samples containing more than 40 wt % cellulose is twice that for the others.

gram of sample, ΔH_f, thus analyzed are listed together with the T_m data in the left-side column of Table I. The tendency of apparently disproportional reduction in ΔH_f with an increase in cellulose content implies a rapid decrease of the degree of crystallinity of the PVA component due to blending with cellulose, corresponding exactly to the observations in the WAXD profiles. Quantitative estimation of the state of miscibility in the as-coagulated blends will be presented later, in the discussion of the result of the dynamic mechanical testing which is quite sensitive for detection of molecular relaxation phenomena including the glass transition of polymers.

(b) Melt-Crystallized Samples (after First Heating). The result of the second heating scan, where stable DSC traces could be obtained over the whole temperature range of the measurement, is shown in Figure 3. In this figure, a thermogram of a mechanical mixture of the two polymers as a fine powder (particle size 50–100 μm) is also given for comparison with the data of the blends obtained by coagulation from solution. It is now possible to estimate the composition dependence of not only the melting but also the glass transition behavior for a series of cellulose/PVA blends with exactly the same thermal history. In the DSC curve of the PVA homopolymer film, the glass transition is apparent over the temperature range 70–85 °C where there is a clear discontinuity in heat flow which is related to the specific heat. From the midpoint of the discontinuity, the glass transition temperature T_g of the PVA sample was estimated to be 80 °C. Concerning the glass transition of cellulose, several papers reported the T_g values located in the limits 200–260 °C in dielectric, NMR, and other studies.[17-21] In the present DSC study, however, we could observe no clear discontinuity in heat flow due to the glass transition of cellulose before the polymer began to undergo thermal decomposition above ca. 240 °C. In the blends of the two polymers, as the composition increases from 0 wt % up to 60 wt % in cellulose content, the T_g of PVA tends to shift to the higher temperature region and there is a broadening of the width of the transition. This may allow one to consider the system to be more or less partially miscible in the amorphous regions in the corresponding composition range. At cellulose contents of 70 wt % and more, the glass transition of PVA is completely undiscernible in the DSC curves. In contrast, a mechanical blend containing only 20 wt % PVA exhibits a clear glass transition in almost the same temperature range as in the case of the pure unblended PVA sample. These comparative observations strongly suggest that there may be a high level of miscibility in the solution-formed blends rich in cellulose.

Other striking effects caused by blending cellulose with PVA are the depression of the melting temperature and the suppression of the development of crystallinity of PVA. The extent of the T_m depression is more marked in the second scan carried out on the melt-crystallized samples, compared with that in the first scan for the as-coagulated samples (see Table I). This suggests that some kind of interaction between the two polymers becomes more prominent at elevated temperatures near the T_m of PVA. Similar blend effects can be observed in the crystallization behavior examined in the subsequent cooling process, as can be seen from Figure 4. It is obvious here that there are sharp and systematic decreases in the crystallization temperature T_c and the exothermic area with an increase in the cellulose concentration. For the weight fractions of PVA below 0.4, it becomes difficult to discern a crystallization exotherm in the DSC curves. Such explicit depressions of T_m and T_c values were not noted in an almost immiscible system of cellulose/nylon 6 blends prepared by a similar method.[14]

Analogous depression phenomena have previously been found in several polymeric blends exhibiting good miscibility; e.g., blends of poly(vinylidene fluoride) (PVF$_2$) with poly(methyl methacrylate) (PMMA),[22] with poly(ethyl methacrylate),[23,24] and with other amorphous polymers;[25] blends of poly(vinyl chloride) with poly(ϵ-caprolactone),[26] with β-propiolactone series,[27] and with other aliphatic polyesters;[28] and so on.[29-31] Nishi and Wang[22] showed that the melting point depression phenomena of PVF$_2$ observed in the blends with PMMA was explicable in terms of thermodynamic mixing accompanied by an exothermic interaction between a crystalline polymer and an amorphous polymer. The same thermodynamic approach was used by Paul et al.[24,25,28,29] and several other workers.[23,27,30,32] A form of the equation for the melting point depression in crystalline/amorphous polymer blends can be written as follows:[24,28]

$$\Delta T_m = T_m^0 - T_m = -T_m^0(V_{2u}/\Delta H_{2u})Bv_1^2 \qquad (1)$$

where the subscripts 1 and 2 are used to designate the amorphous and crystalline polymer components, respectively, T_m^0 is the melting point of pure crystalline polymer 2, T_m is the melting point of the mixture, v is the volume fraction, V_u is the molar volume of the repeating units, ΔH_u is the enthalpy of fusion per mole of repeating unit, and B refers to the interaction energy density of the two polymers, in practice, related to the thermodynamic interaction parameter χ_{12} by

$$B = RT_m^0(\chi_{12}/V_{1u}) \qquad (2)$$

where R is the gas constant. Equation 1 indicates that a plot of ΔT_m versus v_1^2 should be linear with a zero intercept. In accordance with this suggestion, we made an attempt to make such a plot using the reproducible melting data of cellulose/PVA blends obtained in the DSC study (second scan). As a result the relation given in Figure 5 was obtained, where the solid line was drawn by the least-squares method assuming a linear relationship between ΔT_m and v_1^2. In this plot, for convenience, the values $\bar{V}_1 = 1/1.51$ cm^3/g[33] and $\bar{V}_2 = 1/1.29$ cm^3/g[34] were used as the specific volumes of cellulose with extremely low

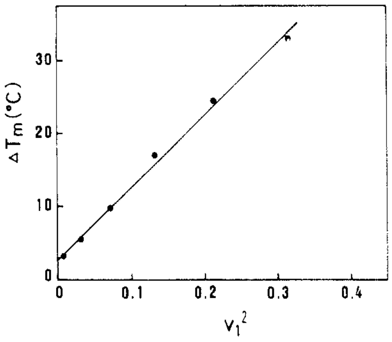

Figure 5. Depression of melting point of PVA in cellulose/PVA blends as a function of volume fraction of cellulose, plotted according to eq 1 (see text).

crystallinity and PVA, respectively, in order to convert weight fractions into volume fractions. The straight line, which fits the observed values well, yielded a slope of 98.2 °C and an intercept of 2.9 °C. The deviation of 2.9 °C from the origin is not far beyond the usually observed limits 0.5–2.5 °C attributed to a residual entropic effect.[24,25,28] On the other hand, the value 98.2 °C of the slope seems to be rather large in comparison with the data obtained for other systems.[22-25,29] Unfortunately, there is no available literature value of the latent heat of fusion of 100% crystalline PVA (ΔH_{2u}) to our knowledge. It is thus impossible at present to precisely assess the value of the parameter B. As a rough estimation, however, taking into account that the crystallinity of PVA films cast from solutions was generally estimated to be 35–60%[35,36] (varying with the conditions of their thermal history) and that we have a ΔH_f value of 25.1 cal/g for a PVA film cast from an aqueous solution at 60 °C, the interaction energy density B may be predicted to assume a value in the range −10 to −18 cal/cm^3. This B value is roughly 2–6 times larger than those specified in literature[22-24,29,37] for other polymer pairs.

The above tentative discussion, based solely on a thermodynamic effect, leads to the conclusion that there is a high degree of interaction between molten PVA and amorphous cellulose molecules. If this is so, the DSC melting result ($\Delta T_m < 4$ °C, see Table I) for the mechanical mixtures of cellulose and PVA once melt-crystallized can be reasonably explained. As indicated previously, the samples were a mixture of powders with particle sizes ranging from 50 to 100 μm, and thus both component molecules might intermix only in interfacial regions between the different domains, presumably owing to the insufficient diffusion of PVA molecules into the cellulose domains under the conditions imposed in this study. However, it should be noted here that a melting point depression may also be caused by morphological effects[22,24,31,37-40] such as the lowering of the crystalline perfection and/or size of the crystallizable polymer, possibly enhanced by the presence of the other component in the blends. The contribution of such morphological effects may be examined explicitly by using samples crystallized isothermally at various temperatures from the molten state of PVA in the blends with cellulose, as has been done for other blends in a few investigations.[22,37,40] Further study, including the precise quantification of the kinetic effect of cooling on the compatibility of the blend pair, is to be conducted for this system.

Dynamic Mechanical Characterization. The results of dynamic mechanical measurements for the solution-coagulated cellulose/PVA films are given in Figures 6–8. Parts a and b of Figure 6 show the temperature dependence of tan δ and E' and E'', respectively, for a pure PVA film and 20/80 and 40/60 blend samples. The dynamic mechanical properties of PVA have been previously investigated in detail mainly for water-cast films by Takayanagi et al.[35,36] They concluded that as many as five mechanical dispersions are observable in this polymer, centering around −60 °C, 35 °C, 80 °C, and two other temperatures above 100 °C. The dispersions observed above 100 °C are due to the crystalline relaxations of PVA and appear as two split peaks in the tan δ versus temperature curve, one peak centering around 135 °C (β_c dispersion) and the other one centering above 180 °C (α_c dispersion). However, the clear separation of the α_c and β_c dispersions is restricted to PVA films with a high degree of crystallinity (>50%). In contrast, PVA films with a relatively low crystallinity (<45%) show a single, large, and broad tan δ peak at ca. 140 °C whose position shifts to the higher temperature side with increasing crystallinity, accompanied by a slight generation of the β_c dispersion as a small shoulder at 135 °C. The dispersions located at about 80 and 35 °C were explained as due to relaxations in the amorphous regions of PVA. That is, the former is the primary dispersion α_a corresponding to the glass transition of PVA and the latter is the β_a dispersion due to the local relaxation mode of the PVA main chains. Finally, a very weak and broad transition centering around −60 °C was attributed to effects of water, which would be obscured in the present study carried out above ca. −60 °C and thus is not considered in the discussion below.

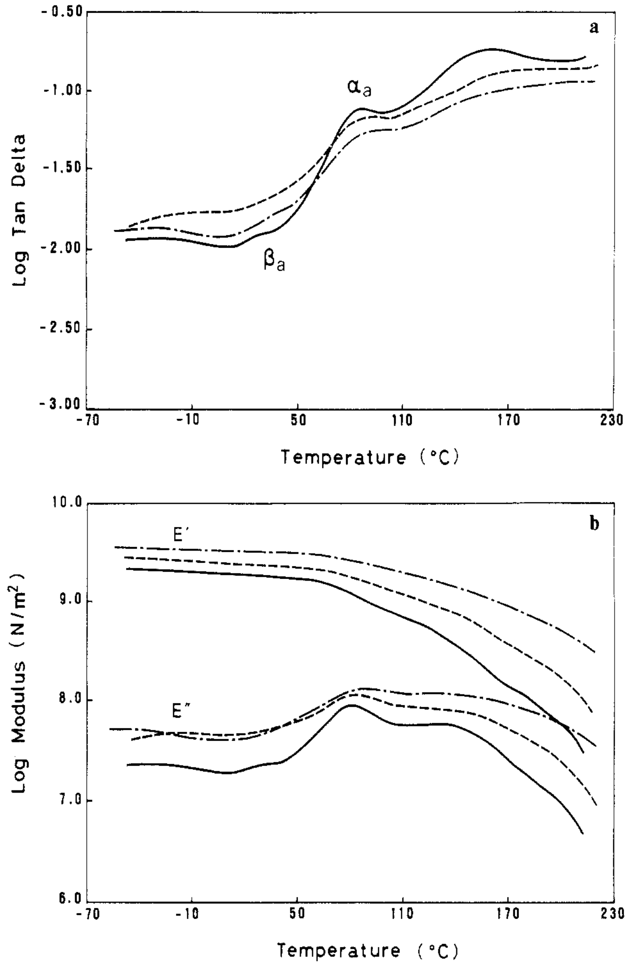

Figure 6. Temperature dependence of (a) the mechanical loss tangent (tan δ) and (b) the dynamic storage modulus (E') and loss modulus (E''), for samples containing 100–60 wt % PVA. Cellulose/PVA: (—) 0/100; (- - -) 20/80; (–-–) 40/60.

In the PVA sample prepared in the present work, three mechanical dispersions appear above 0 °C. The designa-

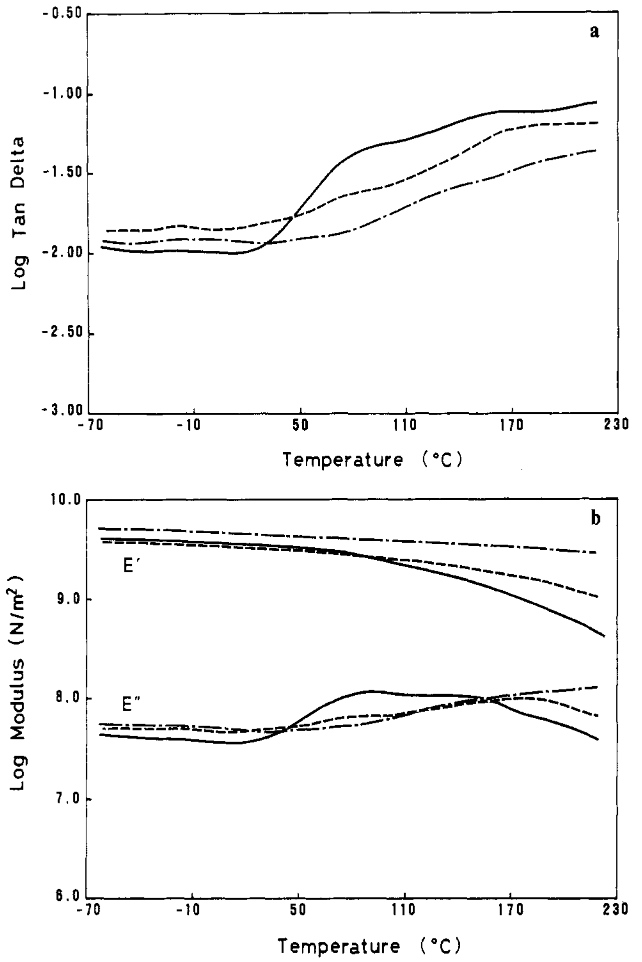

Figure 7. Temperature dependence of (a) tan δ and (b) E' and E'', for a cellulose film and cellulose/PVA blends of 50/50 and 60/40 compositions. Cellulose/PVA: (—) 50/50; (---) 60/40; (–·–) 100/0.

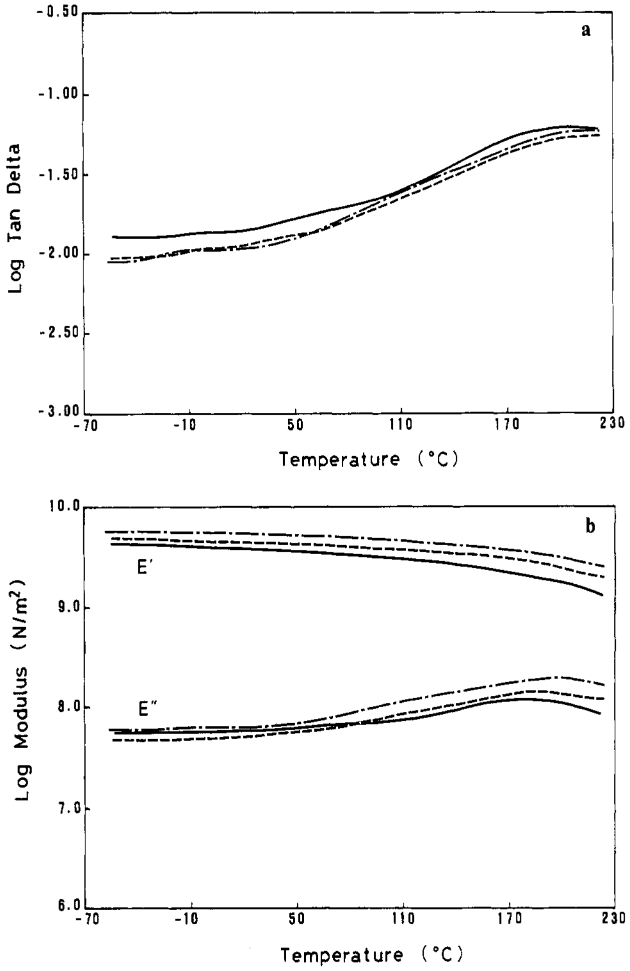

Figure 8. Temperature dependence of (a) tan δ and (b) E' and E'', for samples containing 70–90 wt % cellulose. Cellulose/PVA: (—) 70/30; (---) 80/20; (–·–) 90/10.

tion of each dispersion can easily be done on the basis of the observations made by Takayanagai et al. mentioned above. A sharp peak in tan δ in the neighborhood of 85 °C can be assigned to the α_a dispersion associated with the glass transition, where the micro-Brownian motion of the molecular chains becomes conspicuous in the amorphous regions. In the corresponding temperature region, the dynamic modulus E' decreases markedly from the frozen modulus and a peak in the loss modulus E'' occurs with the maximum at 78.5 °C which is somewhat lower than that (84.5 °C) in the tan δ maximum. The presence of the secondary dispersion β_a is also noted at about 30 °C as a small shoulder in both tan δ and E'' curves. The other dispersion that appears at a temperature higher than the α_a dispersion is concerned with a relaxation in the PVA crystalline phase. This single broad transition peak centered at ca. 150 °C, when expressed with tan δ, may indicate a relatively low degree of crystallinity of this PVA sample. When 20 or 40 wt % cellulose is blended with PVA, the β_a dispersion of PVA becomes suppressed, and the positions of the α_a peaks in tan δ and E'' shift to the higher temperature side, but by less than 10 deg. This behavior implies that the local relaxation of PVA main chains becomes restrained and the glass transition temperature T_g is elevated to some degree by adding cellulose. Quantitative estimates indicated that the α_a peak maxima in tan δ and E'' occur at respectively 89 and 82 °C for the 20/80 sample, and similarly at 93 and 85.5 °C for the 40/60 sample. The crystalline dispersion of PVA loses its prominence as a peak by blending cellulose, which is more clearly seen in tan δ, in accordance with the fact that the PVA crystallinity becomes less with increasing cellulose content, as already elucidated in the WAXD and DSC study. The peak position also apparently shifts to the higher temperature region, but this is probably due to an overlapping of a monotonical increase in tan δ, characteristic of cellulose, in the temperature range 100–220 °C (see Figure 7).

The observed tendency of the gradual disappearance of the PVA viscoelastic profile in the blends continued until the cellulose content reached 50 wt %. In Figure 7, the temperature dependence of tan δ, E', and E'' is shown for cellulose/PVA blends with the compositions 50/50 and 60/40 and, for comparison, for a regenerated cellulose sample which did not show any noticeable relaxation peak in the range 0–220 °C except for faint shoulders located at ca. 50 and 130 °C in the tan δ curve. In the E'' versus temperature curve of the 50/50 sample, we find a peak maximum of the primary dispersion at 87 °C. The corresponding dispersion in the tan δ curve appears to be located with the center at about 95 °C. When the cellulose content increases up to 60 wt %, there is an obviously drastic suppression of the dispersion which has so far been reasonably treated as a main relaxation reflecting the glass transition of each sample. In addition another dispersion, clearly appearing in the E'' curve, is more pronounced at about 175 °C. In interpreting these effects, caution should be exercised because of the melting point depression of PVA which was observed for the blends in the DSC study (see Figure 2). The dispersion observed at ca. 175 °C in the 60/40 sample might have manifested itself so strongly

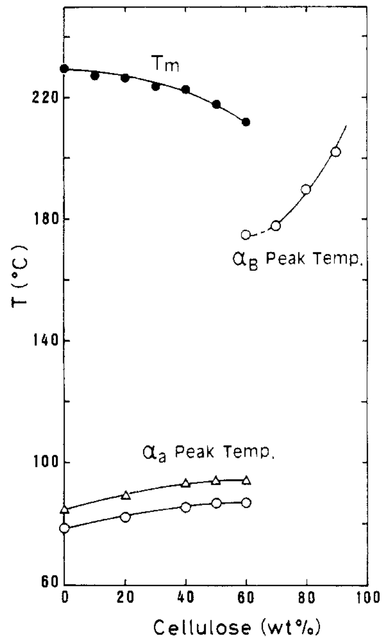

Figure 9. Composition dependence of the melting temperature (T_m) and the peak temperatures of the α_a and α_B dispersions reflecting the glass transition, for the solution-coagulated cellulose/PVA samples: (○) from E'' peak; (△) from tan δ peak; (●) T_m determined by DSC (first run).

as a result of such a melting effect due to some amount of PVA crystals whose melting point is lower (~210 °C) than that (230 °C) of pure PVA. Even though the melting effect might have contributed to the prominence of the dispersion at 175 °C, it is possible that this dispersion originated partly from a molecular relaxation in the cellulose amorphous regions mixed with a large amount of PVA molecules, because it occurs at a position comparable with that of a principal transition, defined as "α_B" below, in blends containing 70–90 wt % cellulose, which hardly showed explicit crystallinity of PVA in the WAXD and DSC study. In this sense, it seems reasonable to assume that two mixed-composition amorphous phases exist in this 60/40 sample; one is rich in PVA whose molecules are mixed with a limited amount of cellulose, and the other is a phase where both components are well mixed with each other at high concentrations.

The result of dynamic mechanical tests performed on the cellulose/PVA blends containing 70–90 wt % cellulose is shown in Figure 8. Here it is no longer possible to detect a mechanical loss peak between 80 and 170 °C in any of the blends. Instead, there is a broad transition over the range of 170–210 °C, where tan δ levels off or appears as a broad peak, E' decreases relatively rapidly in spite of the small magnitude of the drop, and E'' yields a peak maximum at 178, 190, and 202 °C for the 70/30, 80/20, and 90/10 samples, respectively. The peak position thus varies sensitively depending on the composition, shifting to the side of higher temperature along with the decrease of the PVA component. From these observations, it is more reasonable to assume that the new primary dispersion located above 170 °C, which is termed "α_B" here, reflects a molecular relaxation in the amorphous mixture of cellulose and PVA, i.e., the glass transition of the blends, rather than to assume that it is based on some residual PVA crystalline regions, hardly detectable in DSC and WAXD. Accordingly, we believe there is a great degree of miscibility at the molecular level in the blends containing more than 70 wt % cellulose.

The composition dependence of the principal transition α_a or α_B for a series of cellulose/PVA blends is depicted in Figure 9, where the T_m values obtained in the DSC study (first scan) are also plotted to make clearer the thermal transition behavior of the solution-coagulated samples. The glass transition temperature of cellulose itself cannot be detected in the usual viscoelastic measurements before appreciable thermal degradation begins to occur, as was observed in the present work. However, the result of a cellulose sample shown in Figure 7 and the plot of the α_B peak temperatures of the blends with PVA enable us to predict the cellulose T_g to be above at least 230 °C, consistent with our previous estimate.[7] In other mechanical relaxation studies of regenerated cellulose, a T_g value of ca. 250 °C was reported in a torsional braid analysis.[19] Also, quite recently Manabe et al.[21] observed a broad, principal transition centered at ca. 240 °C in the tan δ measurement with a Rheovibron viscoelastomer by using a high rate of heating (12 °C/min) up to 330 °C.

Conclusions

Cellulose/PVA blend films can be easily prepared over the whole composition range from solutions in DMAc–LiCl by the coagulation method described in this work. By visual inspection and optical microscopic observation, there is no indication of phase separation in any of the blends. The WAXD and DSC study revealed that the PVA crystallinity decreases drastically with increasing cellulose content and at cellulose contents of more than 70 wt % the PVA component exhibits no tendency to crystallize. The other component, cellulose, shows a very low degree of crystallinity even in the pure film.

Judging from the result of dynamic mechanical testing, the solution-coagulated blends are not totally miscible at low and intermediate cellulose content (<60 wt %), although there is some level of partial miscibility. At compositions containing 70 wt % and more cellulose, however, it seems reasonable to conclude that the blends exhibit a high level of miscibility in the abundant amorphous regions. It is presumed that the interaction based on the hydrogen bonding between the hydroxyl groups of the two polymers aids in the attainment of the relatively good miscibility. The melting point depression of the PVA component observed in the DSC measurement (first scan) supports the presence of such an interaction. In the case where the concentration of cellulose is not sufficiently high, prevalence of crystallization of PVA inevitably results in less miscible systems in the solid state, even though the original blend solutions exhibit a good state of miscibility. This tendency is somewhat similar to results[26,41] reported for solution-cast blends of poly(ϵ-caprolactone) (PCL) with poly(vinyl chloride), where, at higher levels of PCL, crystallization of the polymer prevents the system from realizing a completely miscible state.

Systematic depressions are also observed more notably in the melting and crystallization temperatures of the blends once melt-crystallized in the DSC pan. It is suggested that the thermodynamic interaction between the two polymer molecules may be enhanced above the melting temperature of PVA, although the contribution of some kind of morphological effect remains to be elucidated.

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Miscibility of Poly(acrylonitrile-*co*-styrene) with Poly[styrene-*co*-(maleic anhydride)] and Poly[styrene-*co*-(*N*-phenylmaleimide)]

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ABSTRACT: Miscibility of blends of poly(acrylonitrile-*co*-styrene) with poly[styrene-*co*-(maleic anhydride)] and poly[styrene-*co*-(*N*-phenylmaleimide)] was determined by measurement of their glass transition temperatures by dynamic mechanical testing. It was found that poly(acrylonitrile-*co*-styrenes) are miscible with poly[styrene-*co*-(maleic anhydride)s] and poly[styrene-*co*-(*N*-phenylmaleimide)s] within specific ranges of copolymer composition for each blend. The boundaries between domains of miscibility and immiscibility were expressed by two straight lines intersecting at the origin, where the abscissa and ordinate represent the compositions of the respective copolymers in volume fraction. From the binary interaction model for copolymer mixtures, segmental interaction parameters between the different monomer units were estimated from these data and were found to be positive for all pairs. No attractive interactions were found between the acrylonitrile and maleic anhydride or *N*-phenylmaleimide. Miscibility of these blends is due to a repulsion between the two different monomer units comprising the copolymer.

Introduction

Studies of miscibility in polymer blends have been reported in recent years. It is generally agreed that the thermodynamic basis is an exothermic heat of mixing, since entropic contributions are so small in high molecular weight polymer blend systems. It is suggested that specific intermolecular interactions, that is, hydrogen bonding and $n-\pi$ complex formation, are responsible for the exothermic heat of mixing.[1,2]

Recently, it has been demonstrated that systems consisting of a homopolymer and a copolymer or two different copolymers are miscible for a certain range of copolymer composition even though the combinations of their corresponding homopolymers are immiscible. It has been proposed that miscibility of copolymers is due to a repulsion between the two different monomer units comprising the copolymer,[3-5] and in a meanfield approach the overall Flory–Huggins interaction parameter between the two polymers can be simply expressed in terms of the respective segmental interaction parameters. ten Brinke et al.[4] extended this formulation to mixtures of two different copolymers. Paul and Barlow[5] and Shiomi et al.[6] applied it to blends of two random copolymers having a common monomer.

There have been many studies of miscibility of poly(acrylonitrile-*co*-styrene) (AS) with a homopolymer and

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