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Cellulose/Poly(vinyl alcohol) Blends: An Estimation of Thermodynamic Polymer–Polymer Interaction by Melting Point Depression Analysis

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In a previous paper[1] of this series relating to cellulose/synthetic polymer blends,[1-3] two of the authors (Y.N. and R.S.M.) reported the preparation of blends of cellulose with poly(vinyl alcohol) (PVA) by a solution-coagulation method using the solvent *N*,*N*-dimethylacetamide (DMAc)–lithium chloride (LiCl). In addition, the characterization of the binary blends, mainly through thermal analysis and dynamic mechanical testing, was described. From the estimation of the glass transition temperature, it was found that the blend system exhibited a high level of miscibility in the abundant amorphous regions, especially at the compositions above 60 wt % in cellulose content. The good state of miscibility was presumed to be due to the 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 the PVA component observed by differential scanning calorimetry (DSC). An attempt was made to analyze the reproducible melting data of cellulose/PVA blends obtained in the DSC heating cycle by using an equation for the melting point depression in crystalline/amorphous polymer blends,[4,5] which was derived from Scott's theory[6] for thermodynamic mixing of two polymers. The tentative discussion based solely on the thermodynamic effect led to the conclusion that there was a high degree of interaction between molten PVA and amorphous cellulose molecules; that is, the polymer–polymer interaction energy density, B, was predicted to assume a large negative value, ca. −10 cal/cm^3 or more in absolute value, as a rough estimation. In the interpretation of that result, however, caution should be exercised since a melting point depression may also be caused by morphological effects[4,5,7-13] such as the lowering of the crystalline perfection and/or size of the crystallizable polymer, possibly varying with composition in the blends. The contribution of such morphological effects, which has remained to be considered further for the cellulose/PVA system, may be examined explicitly using samples crystallized isothermally at various temperatures from the molten state of PVA in the blends with cellulose, as has been done for other systems.[4,7,13-21] The purpose of the present study is to reestimate more quantitatively the thermodynamic interaction between the two polymer components after removal of the contribution of the morphological effects.

Experimental Section

The polymer materials used were the same as specified in the previous paper;[1] i.e., the cellulose sample was a wood pulp with a degree of polymerization of 935, and the other polymer, poly(vinyl alcohol) (PVA) (MW 78 000; 99.7 mol % saponificated), was purchased from Polyscience, Inc. Cellulose/PVA blends were prepared from mixed polymer solutions in *N*,*N*-dimethylacetamide (DMAc)–lithium chloride (LiCl) according to a coagulation method described earlier.[1-3] Blend films with compositions of 0/100, 10/90, 20/80, 30/70, and 40/60 in weight ratio of cellulose/PVA were employed for the following experiments with a Perkin-Elmer DSC-4 apparatus.

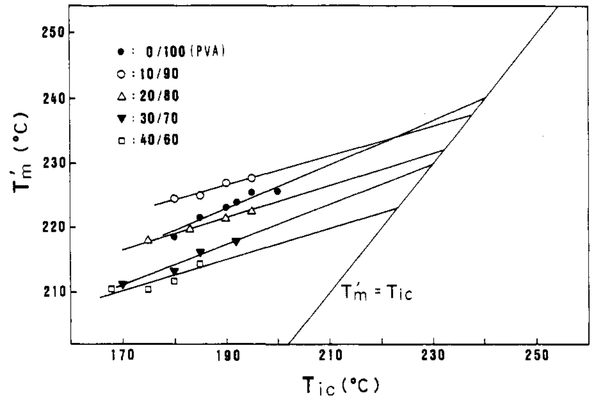

Figure 1. Hoffman–Weeks plots for isothermally crystallized PVA and cellulose/PVA samples.

Table I
Values of Equilibrium Melting Temperature (T_m^{eq}) and Stability Parameter (ϕ) of the Crystals, Estimated from the Hoffman–Weeks Plots for Cellulose/PVA Samples

cellulose/PVA	ϕ	T_m^{eq}, °C
0/100	0.338	240.1
10/90	0.232	237.5
20/80	0.244	232.0
30/70	0.314	229.9
40/60	0.235	223.2

Film specimens, each weighing 7–10 mg, were introduced into aluminum sample pans, heated to 247 °C, and maintained at that temperature for 7 min to completely eliminate PVA crystalline residues before quenching to the desired crystallization and heat-treating temperature, T_{ic}. The samples quenched to T_{ic} were then held at this temperature in the nitrogen-purged DSC cell for about 9 h to allow for complete crystallization. In a subsequent cooling run to 40 °C, it was ascertained that the samples showed no evidence of secondary crystallization. For the samples thus isothermally crystallized, melting temperatures were measured at a heating rate of 20 °C/min. The melting point, T_m', of each sample was taken as the maximum in a single endothermic peak, where any other peaks, e.g., those due to reorganization of already formed crystals during heating, were not observed. The temperature readings were calibrated with pure indium.

Results and Discussion

The variation of the observed melting temperature, T_m', with the crystallization temperature, T_{ic}, examined by DSC for plain PVA and cellulose/PVA blends rich in PVA is presented in Figure 1, depicting the Hoffman–Weeks plot.[10] The experimental data may be fitted by[4,9,10]

$$T_m' = \phi T_{ic} + (1 - \phi) T_m^{eq} \qquad (1)$$

where T_m^{eq} is the equilibrium melting point, and ϕ is a stability parameter[4] which is usually related to morphological factors concerning perfection and size of the crystal. As shown in Figure 1, the values of T_m^{eq} for PVA and its blends with cellulose can be obtained by the extrapolation procedure using a least-squares fit of the data by eq 1 to the intersection with $T_m' = T_{ic}$. The T_m^{eq} values thus estimated are compiled as a function of blend composition in Table I, together with values of the parameter (ϕ) determined from the slope of each straight line. A depression in T_m^{eq} is evidently observed for all the blends investigated here, and the magnitude of the depression increases with increasing cellulose content. The ϕ values, ranging from ca. 0.23 to 0.34, are comparable to those found in recent investigations[14,15,17,19,21] for several other polymer blend

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pairs. It should be noted, however, that the stability parameters (ϕ) for the cellulose–PVA blends are smaller than that for pure PVA. This may be interpreted to mean that the crystalline regions of PVA formed in the blends are larger and more perfect than in the case where the other component cellulose is absent. Actually it is of interest to see in Figure 1 that the observed melting temperatures of the 10/90 cellulose/PVA samples are higher than those of pure PVA when compared at a given T_{ic} in the range analyzed, but the extrapolated lines for both series of the samples cross mutually at a higher T_{ic}, resulting in a depression of T_m^{eq} of the blend. A similar tendency of the explicit decrease in ϕ value for a crystallizable component by blending another polymer can be seen in a few systems[13,15,18,19] studied by using the Hoffman–Weeks approach. At present, we have no complete explanation for such an unexpected blend effect on the change in ϕ. The detailed elucidation is not the main purpose of this paper; yet there is the possibility that the observed behavior is due to a difference in nature of the surface of the cyrstals, rather than to a change in size of the crystalline regions, as suggested by Plans et al.[15] for isotactic polystyrene/poly(2,6-dimethylphenylene oxide) blends.

The equilibrium melting point depression observed above may be primarily ascribed to the diluent effect of amorphous cellulose molecules and can be treated using a thermodynamic approach based on polymer–polymer mixing accompanied by an exothermic interaction between the two components. In this case, a form of the equation for the melting point depression can be written as follows:[4,5]

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

where the subscripts 1 and 2 are used to designate the amorphous and crystalline polymer components, respectively, T_m° is the melting point of pure polymer 2, T_m is the melting point of the blend, 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 characteristic of the polymer pair and is, in practice, related to the thermodynamic interaction parameter χ_{12} by

$$B = RT_m^\circ(\chi_{12}/V_{1u}) \qquad (3)$$

where R is the gas constant.

By use of the T_m^{eq} data given in Table I, a plot of the melting point depression, ΔT_m, versus the square of the volume fraction of cellulose, v_1^2, was constructed as shown by the open circles in Figure 2, where the broken line was drawn by the least-squares method assuming a linear relationship between ΔT_m and v_1^2. In this plot, the values $\bar{V}_1 = 1/1.51$ cm^3/g[22] and $\bar{V}_2 = 1/1.27$ cm^3/g[23] were used as the specific volumes of cellulose with extremely low crystallinity and PVA, respectively, to convert weight fractions into volume fractions. The previous data[1] obtained without removng the morphological effects were also replotted for comparison in the figure by filled circles with a solid line drawn by the least-squares fit. The broken line based on the present data yielded a slope of 106 deg and a positive intercept of 3.0 deg, which are interestingly comparable to the previous result, a slope of 98.2 deg and an intercept of 2.9 deg. The deviation of 3.0 deg from the origin is not far beyond the usually observed limits, 0.5–2.5 deg, attributed to a residual entropic effect,[5,24,25] which was neglected in the derivation of eq 2. From the slope of such ΔT_m versus v_1^2 plots, we can assess values of the parameters B and χ_{12} by eq 2 and 3, in combination with the other necessary quantities described below.

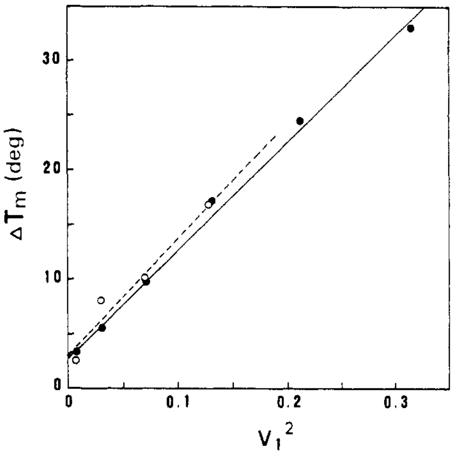

Figure 2. Melting point depression, ΔT_m, as a function of the square of volume fraction of cellulose, v_1^2, for cellulose/PVA blends: (○) data in the present work; (●) data from ref 1. The broken and solid lines were drawn using a least-squares fit of the present and previous data, respectively.

The heat of fusion per unit volume ($\Delta H_{2u}/V_{2u}$) of 100% crystalline PVA was estimated experimentally in the following way: A PVA film was cast from an aqueous solution at ca. 45 °C, and the heat of fusion (ΔH_f) of the sample was measured by DSC. An average value $\Delta H_f = 14.0$ cal/g was obtained in the measurement carried out 3 times. On the other hand, the density (d) of the same sample was 1.298 g/cm^3, which was determined with a density gradient column using a mixture of carbon tetrachloride and n-heptane. Then the degree of crystallinity (X_c) of the film can be calculated as $X_c = 0.413$ (41.3%), using $d = 1.298$ g/cm^3 and the values[23] $d_c = 1.34$ g/cm^3 and $d_a = 1.27$ g/cm^3, according to

$$1/d = X_c/d_c + (1 - X_c)/d_a \qquad (4)$$

where d_c and d_a are the densities of the crystalline and amorphous regions of PVA, respectively. The thus obtained values of ΔH_f and X_c yield $\Delta H_f^\circ = 33.9$ cal/g for the enthalpy of fusion of 100% crystalline PVA. Converting this into a value per unit volume, we obtain $\Delta H_{2u}/V_{2u} = \Delta H_f^\circ d_c = 45.4$ cal/cm^3.

By use of the value of $\Delta H_{2u}/V_{2u}$ and a slope of 106 deg for the ΔT_m versus v_1^2 plot, the thermodynamic interaction parameters are evaluated as $B = -9.38$ cal/cm^3 and $\chi_{12} = -0.985$ (at 513 K); here $V_{1u} = 107$ cm^3/mol, calculated from the molar mass (162.1) and a density of 1.511 g/cm^3 for cellulose, was adopted. Additionally the use of the other slope, 98.2 deg, leads to $B = -8.86$ cal/cm^3 and $\chi_{12} = -0.948$ (at 503 K).

Thus, the thermodynamic interaction parameters B and χ_{12} assume large negative values for the present polymer pair, for example, the B's estimated above being in any event ca. 1.5–4 times as large as those specified in the literature[4,5,7,18,26,27] for other polymer pairs. This result strongly suggests again the presence of favorable interactions possibly due to the hydrogen bonding between the two different polymers. It may also be deduced that such an interaction contributes to enhancement of the state of miscibility in the present blend system.

Registry No. PVA, 9002-89-5; cellulose, 9004-34-6.

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Communications to the Editor

Study of the $T(1)$ Transition of Poly[bis(trifluoroethoxy)phosphazene] Using Solid-State Nuclear Magnetic Resonance Spectroscopy

Considerable interest has been developed in thermotropic polymers generally over the past decade or more.[1-3] In semicrystalline polyphosphazenes three transitions have been established: glass temperature T_g, thermotropic (mesophase) transition $T(1)$, and melting transition, T_m. Whenever the side-group chemistry is altered, these parameters scale linearly[4] in a plot of $(T_m - T_g)/(T_m - T(1)$ against $T(1)/T_m$. The first-order transitions $T(1)$ and T_m are well-known for poly[bis(trifluoroethoxy)phosphazene] (PBFP),[3] typically $T(1) \sim 85$ °C and $T_m \sim 242$ °C. T_g lies well below these transitions at approximately −66 °C. Interestingly, there is a significant change in the location and magnitude of the $T(1)$ transition whenever polyphosphazenes are heated and cooled. In PBFP specifically crystallized from solution, samples are usually spherulitic. Small-angle X-ray measurements made on crystal mats formed at room temperature indicate that lamellae of ~ 140 Å are obtained. The crystallinity of these specimens is suprisingly low (<50%) and the crystal structure is monoclinic. When heated through $T(1)$ the sample undergoes some form of chain extension. The thermotropic state is comprised of molecules hexagonally packed in arrays or domains. In this condition they have considerable fluidity as creep and other measurements substantiate.[5] The interchain spacing has been assessed by X-ray and electron diffraction,[6] which confirms the hexagonal arrangement in the 2D δ-state.[6,7] Whenever PBFP is cooled from the molten state it returns very rapidly to the 2D hexagonally packed phase and finally crystallizes into a 3D orthorhombic structure below $T(1)$ (i.e., different from the original monoclinic form). [After the first thermal cycle through $T(1)$, the 3D orthorhombic phase dominates below $T(1)$.] Apparently the transformation occurs through relatively small displacements or translations in the chain direction so as to allow growth to occur laterally with an Avrami[8] $n = 2$. The crystallinity of PBFP returned to room temperature is much higher than the starting specimen and the location and enthalpy of the $T(1)$ transition is increased substantially upon thermal cycling. The chain packing and the resultant 3D ordering shows that $T(1)$ and $\Delta H[T(1)]$ asymptotically approach an upper limit in PBFP and in other polyphosphazenes.[3] Dilatometry measurements[5] clearly indicate the first-order nature of $T(1)$ and T_m as well as a significant volume change ($\sim 6\%$) that is associated with material expansion and enhanced mobility that occurs at both of these temperatures.

Wide-line nuclear magnetic resonance (NMR) and X-ray measurements were made on PBFP about a decade ago.[9] It was reported that the thermotropic state of this polymer is involved with rapidly rotating chains in a hexagonal lattice that exhibited both lateral order and longitudinal disorder. This condition or state was attributed to the onset of rapid side group and backbone chain motions.

Now that solid-state NMR has emerged as a technique for studying local molecular dynamics and conformational changes through decoupling side group and main-chain motions, its application to polyphosphazenes is not surprising. The first high-resolution solid-state NMR study of polyphosphazenes was reported only 1 year ago by Crosby and Haw.[10] ^{31}P magic-angle spinning (MAS) NMR was used to examine the hydrolysis and cross-linking of poly(dichlorophosphazene). The molecular dynamics of poly(dimethyloxyphosphazene) (PBMP) and poly(diethoxyphosphazene) (PBEP) was studied by ^{31}P MAS and ^{13}C cross-polarization (CP)/MAS NMR at various temperatures. The results from this investigation indicate that the main chains of PBEP and PBMP are undergoing large-amplitude anisotropic motions above their respective glass transition temperatures. Crosby and Haw concluded that ^{31}P MAS and ^{13}C CP/MAS NMR can be used to study molecular dynamics in phosphazene polymers.

More recently Tonelli and co-workers[11,12] investigated the phase transitions of poly[bis(*p*-ethylphenoxy)phosphazene] (PBEPP). They used ^{31}P MAS/dipolar decoupling (DD) at several temperatures and found a sudden decrease in line width corresponding to the crystal–liquid crystal transition which occurred above 100 °C. They concluded that considerable backbone motion occurs whenever PBEPP passes into the thermotropic phase. From the spin–lattice relaxation times, T_1 of the carbon atoms on the side group, they reported that the side chains were also mobile in the thermotropic phase. According to this work, short spin–lattice relaxation times observed only for the protonated aromatic carbons in the 3D crystal indicate that phenyl rings are mobile and rotating about their 1,4-axes even below the $T(1)$ transition.

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