Correlation between the Degree of Phosphorylation of Poly(styrenephosphonate ester) and Its Blends with Cellulose Acetate

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ABSTRACT: Phosphorylated polystyrene derivatives (PSP), in the form of random copolymers of styrene/styrenephosphonate diethyl ester and poly(vinylbenzylphosphonate ester), have been blended with semicrystalline cellulose acetates. Correlation between the degree of phosphorylation and miscibility of the PSP/CA blends is presented. Differential scanning calorimetry studies reveal a single glass transition temperature for blends consisting of more than one phosphoryl group per four styrene units. A significant melting temperature depression with the augmentation of a PSP fraction in the blend is observed; crystallization of CA seems to be completely impeded in the presence of more than 30 wt % PSP. The rate at which T_m decreases is shown to depend largely on the degree of phosphorylation of the PSP grades. Negative values of the interaction parameters χ were calculated for the miscible polymer pairs from melting temperature depression data using Hoffman-Week's plots to determine equilibrium - T_m. The values of χ are shown to be strongly dependent on the volume fraction of PSP in the blend, as well as on its degree of phosphorylation. Some infrared spectroscopy data supporting these findings are presented. Two CA grades containing ~2.5 acetyl but with different distributions of the primary and secondary hydroxyl on the glucose units are used; both variations are shown to yield quite similar results. Relevant characterizations of the parent polymers are also reported.

Introduction

Polymer pairs containing phosphorylated derivatives of polystyrene in the form of poly(styrenephosphonate diethyl esters) (PSP), and cellulose acetate (CA) derivatives, were reported miscible in solution and in solid.[1,2] It was shown recently[3,4] that spontaneous mixing occurs in semicrystalline heterogeneous blends, prepared from these types of pairs, when annealed above the glass transition temperature of CA, yielding a wholly amorphous blend with a single T_g. In these PSP/CA blends, cellulose acetate is the semicrystalline component with a T_m of ~233 °C (peak point) and a T_g of ~190 °C, which is at least 100 °C higher than that of the amorphous PSP derivatives.[3]

The inability of CA to recrystallize in the presence of PSP, when annealed for several hours at the temperature range $>T_g$ to $<T_m$, suggested that relatively strong interactions prevail between this class of polymer pairs. These specific interactions have been assumed to be primarily related to hydrogen bondings between the hydroxyl moieties of CA and the phosphoryl groups (P=O) of PSP.[5,6] This imparts unusual complexity to this blend system for several reasons. As shown in Table I, the cellulose acetate contains two types of residual hydroxyl groups, primary and secondary, which differ not only in their chemical nature but also in their accessibility. The primary hydroxyl is the more accessible and is the better candidate for interaction. However, the information concerning the distribution of these hydroxyl groups in CA is quite tenuous; in fact, cellulose acetate is only a generic designation assigned to a family of acetylated cellulose having about five acetyl groups per two glucose units. Depending upon the acetylization procedure, the CA can be rich in either primary or secondary hydroxyl groups and may also have large triacetate segments (i.e., three acetyl residues per glucose unit), which are less likely to interact with PSP. Such segments crystallize readily even in the presence of large fractions of PSP in the blend.[5] A preliminary screening of commercially available cellulose acetate grades revealed that all are miscible with PSP.[1-5] The fact that high molecular weight PSP (>200 000) proved miscible with CA even at relatively high temperatures (ca. 260 °C) where degradation of CA takes place[3] prompted us to conduct a quantitative thermal analysis of the PSP/CA blends. This, however, requires some proper understanding of the thermal behavior of the cellulose acetate grade in use; the lack of such relevant data in the technical literature for this class of commercially important polymers is conspicuous. This paper provides some of this necessary data.

Finding a correlation between the degree of phosphorylation of PSP and its miscibility with CA is the primary objective of the present study. Since crystalline fractions of CA could be expected in blends containing relatively low volume fractions of PSP, melting temperature depressions[3] have been anticipated and sought for assessment of interaction parameter values, as has been reported for other semicrystalline blends.[7-14] Because the prominent interactions between PSP and CA are believed to involve two different types of hydroxyls, the interaction parameter χ_{AB} was predicted to be concentration-dependent. Therefore, correlations between melting temperature depression and the fraction of PSP in the blends were sought.

Various grades of PSP having different phosphoryl ester content and CA grades were used in the present study. Since substantial amounts of supporting data concerning the parent polymers had to be generated, and are provided herein, this manuscript deals primarily with the interpretations of the thermal analysis results and, to a much lesser extent, with the spectroscopic data. Elaboration on the latter together with TEM data is the subject of subsequent manuscripts.[6]

Besides the apparent interest to establish the ground for a model system that links cellulose derivatives to synthetic polymers via specific functional groups, the PSP/CA blends have been proven to be very effective polymer-membrane matrices.[1,2] Membranes constructed from these blends have been shown to effectively separate organic solvent mixtures (e.g., benzene/cyclohexane) and to com-

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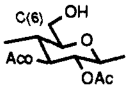
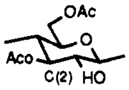
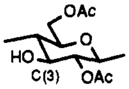
Table I
Pertinent Properties of Cellulose Acetate[a]

sample designatn	acetyl, %	hydroxyl[b] OH %			mol wt (M_w)	density, g/cm^3	T_g,[c] °C	ΔC_p,[d] cal/g·deg
		C(6)	C(2)	C(3)				
CA45	39.4	55.5	9.3	35.2	62 000	1.305	189	0.081
CA3	39.8	38.1	32.2	29.7	29 000	1.312	190	0.083

[a] Product of Eastman Kodak Co. [b] Determined ^{1}H NMR:







[c] T_g value was taken at the midpoint of the heat capacity change of the glass transition. [d] Extrapolated to the wholly amorphous polymer from the plot of ΔH_f vs ΔC_p (see text).

Table II
Characteristics of Poly(styrenephosphonate esters)

designatn	phosphorylation,[a] %	Cl,[a] wt %	M_n[b]	density, g/cm^3	T_g,[c] °C	ΔC_p at T_g, cal/g·deg
PSP-32	32	0.20	68 000	1.112	56	0.062
PSP-39	39	0.14	74 000	1.124	52	0.060
PSP-58	58	2.11	85 000	1.140	51	0.056
PSP-60	60	0.37	88 000	1.141	41	0.055
PSP-87	87	1.10	102 000	1.144	39	0.053
PSP-95	95	0.30	108 000	1.147	35	0.052
PSP-100[d]	100	0.0	147 000	1.144	9	0.050

[a] Determined by elemental analysis. [b] Determined by membrane osmometry with toluene. [c] Taken at the midpoint of the heat capacity change of the glass transition. [d] Polymerized from vinylbenzylphosphonate ester with AIBN.

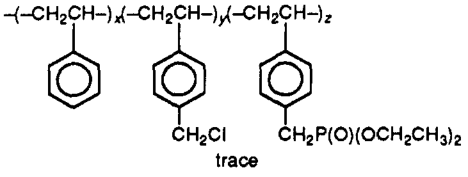
plex and support heavy-metal salts and semiconductors. Therefore, the inherent degree of miscibility of the PSP/CA blends is of great general interest.

Experimental Section

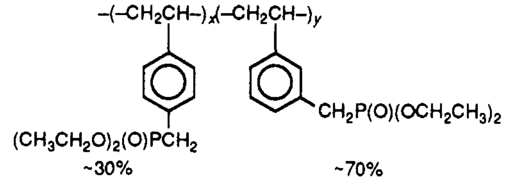
Materials. Two versions of cellulose acetate (CA) [Eastman Chemical Products, Inc.], designated by the manufacturer according to their viscosities, CA45 and CA3, were used. (The numbers are the units, in seconds, determined by the falling-ball viscosity method ASTM-D.) Their properties are summarized in Table I. Polystyrene (PS), standard [Alfa Chemical Co.], with a molecular weight of 47 500 ($M_w/M_n \simeq 1$) and T_g of 104 °C, was used to synthesize poly(styrenephosphonate diethyl ester) (PSP) derivatives. Vinylbenzyl chloride (VBC) was provided by the Dow Chemical Corp. (MI). Reagent-grade *p*-dioxane (J. T. Baker Chemical Co.) was used as the solvent in preparing samples of PSP/CA blends.

Synthesis. The PSP samples were prepared as described in ref 1. In short, chloromethylation of polystyrene (PS) was followed by Arbuzov reaction with triethyl phosphite. Polydentate ether [bis-2-ethoxy ethyl ether (diethyl carbitol)] was used as a diluent in the reaction to impede cross-linking. Completely soluble PSP grades were produced with molecular weights corresponding to that expected from the degree of substitution (Table II). The number-average molecular weight (M_n) was determined by membrane osmometry with toluene as a solvent.

The degree of phosphorylation and amount of residual chloromethyl groups in the PSP samples were determined by elemental analysis (Table II). ^{1}H NMR confirmed that all phosphorylated polystyrene samples prepared by this method contained phosphoryl ester groups in the para position, with the general structure



A grade of fully substituted phosphorylated polystyrene, designated PSP-100, was synthesized from the monomer vinylbenzylphosphonate diethyl ester (VBP), which was prepared by reacting VBC with triethyl phosphite. This variation was produced by radical polymerization using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator.[15] This PSP version contains ca. 70% of phosphoryl ester group in the meta position as confirmed by ^{1}H NMR analysis; as such it is a random copolymer of meta and para isomers



PSP-100

Preparation of CA/PSP Blends. Cellulose acetate and PSP were dissolved separately in *p*-dioxane at concentrations of 5 and 2 wt %, respectively. The two solutions were then mixed in different proportions, yielding homogeneous transparent mixtures, with each blend solution stirred for at least 2 h. About 1 mL of the solution was then transferred to a long-neck glass vial (2-cm diameter) and placed in a desiccator in which the solvent was allowed to evaporate slowly until solid dense isotropic films were formed, usually within 3–4 days. The films were subsequently placed in a vacuum oven at 45 °C for several days until no trace of solvent could be detected by infrared spectroscopy (FT-IR was used). A similar series of blends that were used to determine composition-dependent properties were prepared by the same method, but with solutions of 5 wt % PSP in *p*-dioxane.

Characterization. Densities of the blends were determined by the buoyancy method in aqueous $ZnCl_2$ solution, with the effective column height of 70 cm and a density range of 1.0–1.5. In order to reduce the contribution of the crystalline fraction, the density measurements of pure CA, and blends of PSP-100/CA with a high fraction of CA, were conducted with specimens rapidly quenched from the melt (245 °C) to room temperature prior to measurements.

Differential scanning calorimetry (DSC) thermograms were recorded on a Perkin-Elmer DSC-4, equipped with a thermal analysis data acquisition station. Unless otherwise mentioned, all measurements were conducted under a constant flow of nitrogen at a 20 °C/min scanning rate; the T_g was taken from a second DSC trace following an initial run in which the sample was briefly heated above the melting temperature of CA and rapidly quenched (cooling rate of 300 °C/min). The T_g-midpoint value was taken at the midpoint of heat capacity change (i.e., $\Delta C_p/2$) during the transition. The values of ΔC_p were calculated from the vertical distance between the two extrapolated base lines at T_g. The T_g onset was taken at the intersection of the lower base line with the tangent to the transition curve.

Crystallization of CA was accomplished by heating the semicrystalline samples in the DSC cell above melting temperature (250 °C) followed by a slow cooling (10 °C/min) to a desired crystallization temperature, T_c. The samples were kept at T_c for a required length of time and then cooled to ambient temperature. The melting endotherms were subsequently obtained at a scanning rate of 20 °C/min. Unless specified differently, the melting temperature, T_m, was taken at the point where the tail end and the base line of the endotherm curve connect. Using the

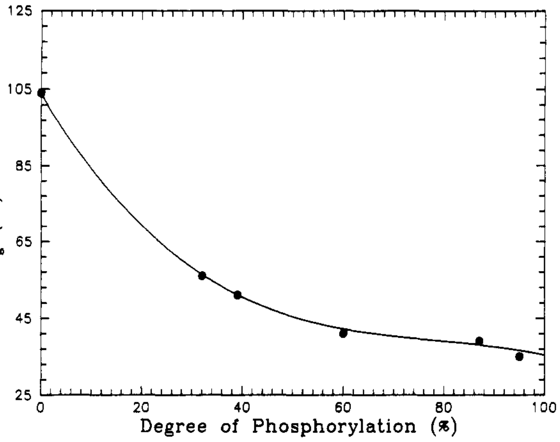


Figure 1. Plot of glass transition temperature (T_g) vs degree of phosphorylation of poly(styrenephosphonate diethyl esters) (PSP).

endotherm's peak as T_m gave overall the same results but with a higher error margin due to the change in the size and curvature of the endotherms (see also ref 13). The peak area was taken as the heat of fusion, ΔH_f, of the crystalline domains.

Infrared spectra were recorded on a Nicolet 20 DX FT-IR spectrophotometer with a resolution of 2 cm^{-1} and a minimum of 25 cumulative scans. Thin films of the blends were coated from acetone solution (0.5 wt %) on a NaCl window that were subsequently dried with an infrared lamp.

Cellulose acetate X-ray diffraction diagrams were recorded in an evacuated, flat-film camera with pin-hole collimation, using Ni-filtered Cu Kα radiation. The film used was CEA Reflex 25. The diffractogram was recorded for 16 h at a film-to-sample distance of 5 cm, with a power setting of 35 kV and 18 mA.

Properties of the Parent Polymers

The properties of the PSP and CA grades used in this study were rigorously studied before characterization of the blends was pursued. A detailed account of the impact of the degree of phosphorylation on the properties of the PSP grades used in the present study was recently published elsewhere.[16] The relevant data concerning the two families of polymers are reported below.

Poly(styrenephosphonate diethyl ester) (PSP). The relationship between the degree of phosphorylation and the thermal properties of the PSP is of special importance to this study. A significant decrease in T_g follows the increase in the degree of phosphorylation (Figure 1). The PSP version that was prepared directly from the monomer (i.e., PSP-100) exhibits much lower T_g (9 °C) than the extrapolated value (~30 °C) for a fully phosphorylated polystyrene, shown in Figure 1; its density values are also slightly lower (Table II). These might be attributed to a lower packing density and greater segmental mobility of this PSP variation that consists of meta and para isomers. It has to be kept in mind, however, that PSP-100 is a product of radical polymerization of the phosphorylated monomer and, thus, possesses a higher molecular weight distribution ($M_w/M_n \sim 1.5$) than the rest of the PSP grades, which were prepared from the monodispersed polystyrene. The progressive depression of both T_g and ΔC_p with the increase of the phosphoryl ester content (Table II) is rather unique.[16] This suggests an expanded conformational freedom of the phosphonate ester group as their content in the polymer increases. The smaller and bulkier intermediate group, $-CH_2Cl$, produces the common opposite trend, i.e., an increase in T_g with a concurrent decrease in ΔC_p.[16] Consequently, residual chloromethyl groups in the PSP were found to have a significant impact on T_g [e.g., as shown in Table II, PSP-58 having ~12% residual chloromethylated groups exhibits a T_g of about 10 °C higher than that of PSP-60]. A comparative analysis between the chloromethylated polystyrene and the PSP is also reported in ref 16.

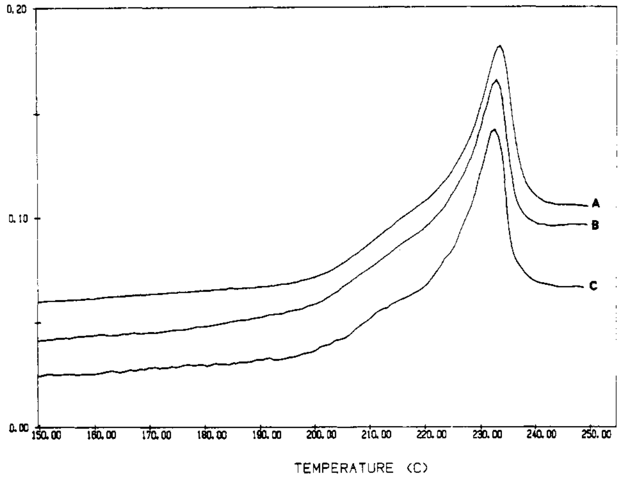


Figure 2. Differential scanning calorimetry thermograms of "as-received" cellulose acetate powder (Eastman CA45). Scanning rate: (A) 20 °C/min; (B) 10 °C/min; (C) 5 °C/min.

Cellulose Acetate (CA). The primary rationale for selecting the CA grades described in Table I for the present study has been the nearly equal division between primary and secondary hydroxyl groups in CA45 and the nearly equal distribution of hydroxyls among the three positions in CA3. Grades that contain only primary or secondary hydroxyl groups were reported to be more heterogeneous, presumably due to the existence of large triacetate blocks.[5]

In spite of the differences between CA3 and CA45, their miscibilities with PSP, as shown below, follow the same trend. Therefore, the relevant experimental data reported here are confined mostly to CA45, while supporting data are provided herein when necessary for CA3. Unless otherwise specified, CA45 is also designated as CA in this text.

The DSC traces of the CA powder (as received) show a sharp melting peak at 233 °C and an ending point at 243 °C (Figure 2). The different scan rates shown, 20, 10, and 5 °C/min, exhibit the same T_m and ΔH_f values. The rather large endotherm, indicative of a highly crystalline fraction, corresponds to a heat of fusion (ΔH_f) of 1.8 cal/g. The surprisingly high degree of crystallinity of the CA powder was confirmed by X-ray diffraction analyses (Figure 3) revealing a crystalline fraction of 50% (±8%). Detailed analysis of the crystalline structure of the cellulose acetate, which can be viewed as a random copolymer of various acetylated glucose units, is not available, and the issue will be addressed elsewhere.[17] Melting endotherms of CA, recrystallized by annealing the polymer in a DSC cell for 10 and 20 min at four different temperatures, are shown in Figure 4. The data (Table III) collected from the DSC traces show an expected increase in T_m and ΔH_f with the increase of annealing time at crystallization temperature. The data indicate faster crystallization at ~215 °C but suggest a higher T_m when annealing is conducted at higher temperatures. As for most semicrystalline polymers, Figures 2 and 4 clearly indicate that the nature of the crystalline phase in cellulose acetate depends on its thermal history. The relatively high degree of crystallinity observed in Figure 2 was previously shown to be a typical outcome of slow precipitation from solution,[5] thus providing larger crystals than those formed via quenching from the melt. The progressive increase in T_m and the degree of crystallinity, with the augmentation of annealing

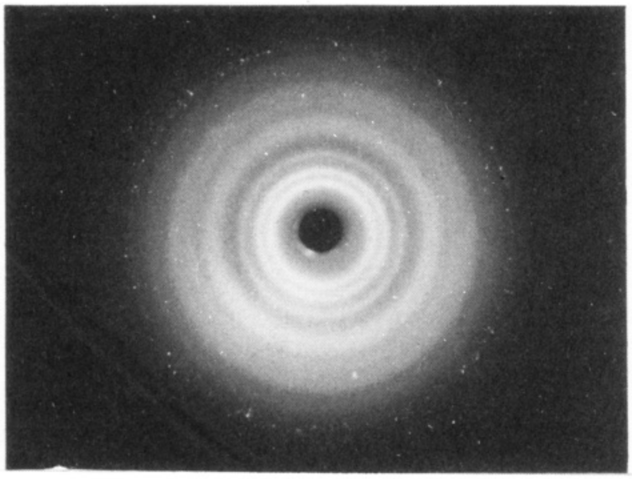


Figure 3. X-ray diffraction pattern of cellulose acetate (CA45) powder.

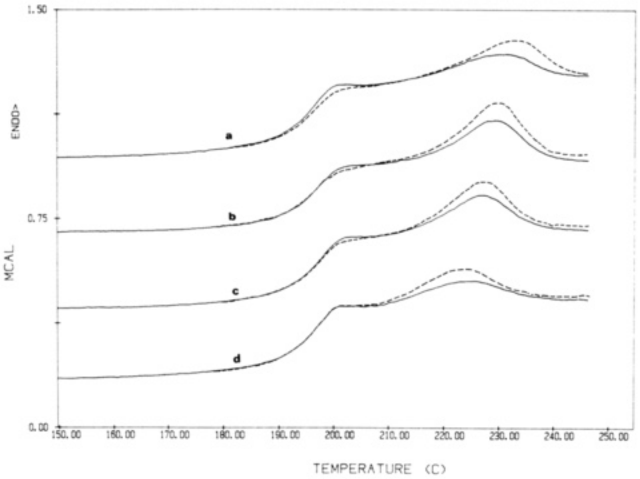


Figure 4. Differential scanning calorimetry thermograms of cellulose acetate crystallized at different temperatures. T_c: (a) 220 °C; (b) 215 °C; (c) 210 °C; (d) 205 °C. Annealing time: 10 min for solid chart and 20 min for dash chart (scan rates of 20 °C/min).

Table III
Melting Temperature and Heat of Fusion of Cellulose Acetate (CA45) at Different Crystallization Temperatures and Annealing Times

T_c, °C	anneal time, min	T_m, °C	heat of fusion (ΔH_f), cal/g	crystallinity,[a] %
205	10	240.2	0.52	20
210	10	241.3	0.65	25
215	10	242.3	0.74	28
220	10	244.5	0.53	20
205	20	241.4	0.61	23
210	20	242.5	0.84	32
215	20	244.0	0.95	36
220	20	245.0	0.75	28

[a] Calculated from the values of the heat capacity change of the samples ($\Delta C_p = 0.081$ cal/g·deg for the wholly amorphous CA).

time, shown in Table III, suggests enlargement of the crystals, but direct measurements of crystallite dimension has yet to be conducted.

Thus, kinetic contributions to the melting endotherms arise in the annealing process (Table III) because crystals are formed at temperatures below their equilibrium melting temperatures, $T_c < T_m$. To circumvent the difficulties of assessing thermodynamic parameters without having to measure the crystal dimension, Morra and Stein[13] have pointed out that it suffices to determine equilibrium melting temperatures employing the Hoffman–Weeks extrapolation method. Such extrapolation to the reference line $T_m = T_c$ yields an equilibrium melting temperature of 253 °C (±0.5 °C) for CA (Figure 5).

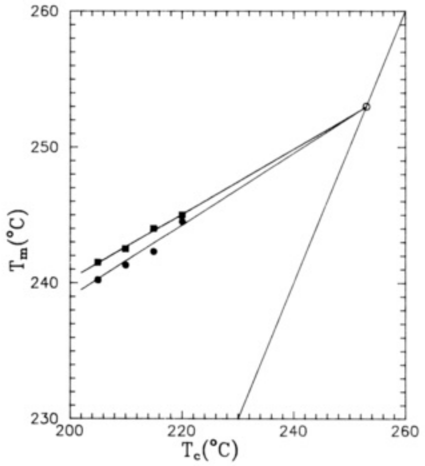


Figure 5. Hoffman–Weeks plots of cellulose acetate (CA45). Annealing time: (●) 10 min; (■) 20 min.

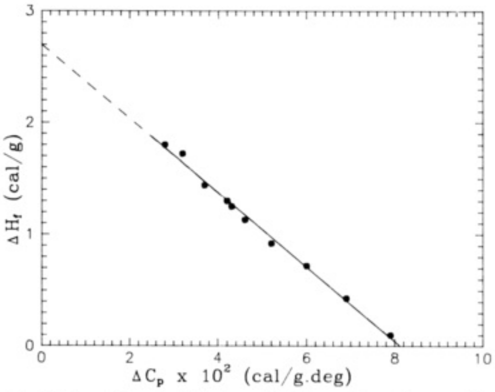


Figure 6. Plots of heat of fusion (ΔH_f) and heat capacity change at T_g (ΔC_p) vs degree of crystallinity of cellulose acetate.

Table IV
Relationship between the Heat Capacity Change and the Heat of Fusion of Cellulose Acetate (CA45)[a]

designatn	heat capacity change (ΔC_p), cal/g·deg	heat of fusion (ΔH_f), cal/g	crystallinity,[b] %
1	0.028	1.80	65
2	0.032	1.72	60
3	0.037	1.44	54
4	0.042	1.30	48
5	0.043	1.25	46
6	0.046	1.13	43
7	0.052	0.92	36
8	0.060	0.72	26
9	0.069	0.43	15
10	0.079	0.10	3

[a] Samples were heated close to T_m of cellulose acetate (CA45), ca. 230 °C (endotherm peak), and then cooled to ambient temperature at a cooling rate of 20 °C/min. [b] Calculated from the values of the heat capacity change of the samples.

The heat of fusion, $\Delta H_f°$, of a wholly crystalline CA was extrapolated from Figure 6, in which a plot of ΔH_f vs the heat capacity change at T_g is shown. This plot is constructed from a series of 10 samples, with different thermal histories, possessing various degrees of crystallinity (Table IV). Since amorphous cellulose acetate recrystallizes relatively slowly upon heating, recrystallization exotherms that would have otherwise interfered with data collection could not be detected in the DSC traces (Figure 2). The degree of crystallinity was also computed from the magnitude of the heat capacity change, ΔC_p, at T_g;

Table V
Thermal Properties and Densities of PSP-100/CA45 Blends

designatn	PSP fraction wt %	PSP fraction vol %	density (ρ), g/cm^3	T_g, °C midpoint	T_g, °C onset	ΔT_g, °C	$\Delta C_p \times 10^2$, cal/g·deg
A	0.0	0.0	1.305	189	183	13	7.9 ± 0.3
B	13.6	15.2	1.285	161	143	39	7.5 ± 0.2
C	27.5	30.2	1.260	132	105	53	7.1 ± 0.2
D	41.2	44.4	1.243	99	85	46	6.8 ± 0.2
E	54.7	57.9	1.220	85	69	40	6.4 ± 0.1
F	68.8	71.6	1.189	58	44	35	6.0 ± 0.1
G	81.4	83.3	1.170	38	26	27	5.7 ± 0.1
H	100.0	100.0	1.144	9	0	22	5.0 ± 0.1

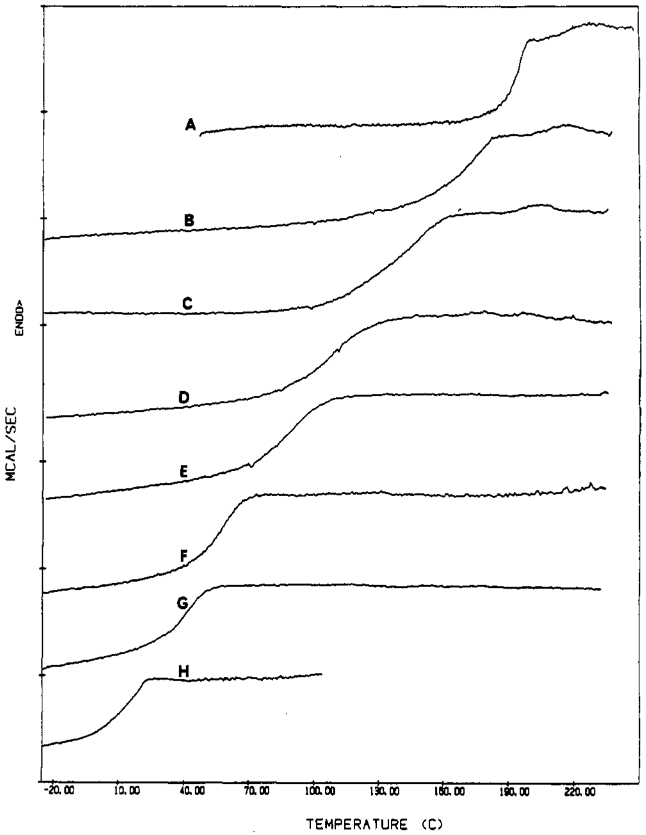


Figure 7. Differential scanning calorimetry thermograms (second run) of PSP-100/CA blends with different compositions. PSP wt %: (A) 0; (B) 13.5; (C) 27.6; (D) 41.3; (E) 55.2; (F) 69.0; (G) 83.5; (H) 100.

this value is shown experimentally to increase proportionally with the content of the amorphous fraction in cellulose acetate (Figure 6 and Table IV). The intercept of the heat of fusion, $\Delta H_f°$, yields a value of 2.7 cal/g at 100% crystallinity (for CA3, the value obtained is ca. 3.0 cal/g). This value cannot be obtained in a direct measurement because a single crystal of CA cannot be found or produced. The ΔC_p of wholly amorphous CA that is extrapolated from the figure yields the exact value (0.081 cal/g·deg) previously reported for this polymer.[3]

Properties of Blends

Composition-Dependent Properties of PSP/CA Blends. Solution-cast blends composed of highly phosphorylated PSP grades (at least one phosphorylester group per two styrene units) are an exceptionally transparent solid, characterized by single glass transition temperatures over the entire PSP/CA composition range. The optical clarity and texture of blends containing up to 70% PSP are indistinguishable from that of pure noncrystalline CA film. Recent measurements[18] have shown that the refractive indices of fully phosphorylated polystyrene, PSP-100, and CA are very close, 1.483 and ~1.475, respectively. In fact, the progressive phosphorylation of polystyrene (n^{20}_D 1.593) leads to a respected decrease in the index of refraction. Microphases can be induced in blends prepared from solution[4] or in the situation if the PSP grades contain less than one phosphoryl ester group per two styrene unit; however, indications that a much lower degree of phosphorylation is required to render true immiscibility to the blend are revealed in the experimental results reported below.

Some thermal properties of PSP-100/CA are given in Table V; the respective DSC thermograms are shown in Figure 7. A single T_g region for each blend composition is observed; a small crystalline melting endotherm of CA is typically found in the first scan of blends containing less than 30 wt % PSP. All blends exhibit a broader T_g span than that of the parent components (ΔT_g in Table V). The traces B–D display relatively larger broadening of the T_g region; this is attributed to melting and conversion of the remaining CA crystallites to the amorphous phase during the first scan; rescanning or annealing the blend at elevated temperature reduces ΔT_g.[4] Note that since CA decomposes slowly above 250 °C,[3] we have elected to analyze this series of blends through the traces of the second DSC scan, thus providing minimum exposure time above T_m.

Plots of T_g versus composition are shown in Figure 8. Both solid (midpoint) and dashed (onset) curves were calculated according to eq 1[19] where W is the weight

$$(1/T_g)_{\text{blend}} = (W/T_g)_{\text{PSP}} + (W/T_g)_{\text{CA}} \qquad (1)$$

fraction of the pure component in the blend. The experimental data shown in Figure 8 are in close agreement with the calculated curves; the onset T_g exhibit a better fit than the midpoint value, which is consistently higher.

Similar plots (not shown here to avoid redundancy) were obtained for blends of cellulose acetate with the highly phosphorylated derivatives PSP-95 and PSP-60. Conversely, phase separation is clearly indicated from the thermograms of the solution-cast blends with PSP-39 and PSP-32. The DSC traces of these blends exhibit two T_g's, as shown in traces A and B in Figure 9, but the polymer components spontaneously mix when annealed above T_g(CA), and ultimately yield a homogeneous phase exhibiting a single T_g, which corresponds to that calculated from eq 1, as shown in Figure 9C. The spontaneous mixing above the glass transition temperature clearly indicates that a much lower content of phosphoryl groups is needed to impart miscibility than that implied from the solution-casting preparation; the rate at which the polymer pair self-mix above T_g has been recently reported.[3,4] It suffices to mention at this point that, for most of the PSP/CA blends, a minimum of one phosphoryl group per four styrene units seems to be needed for completion of such "thermal" blending.[3]

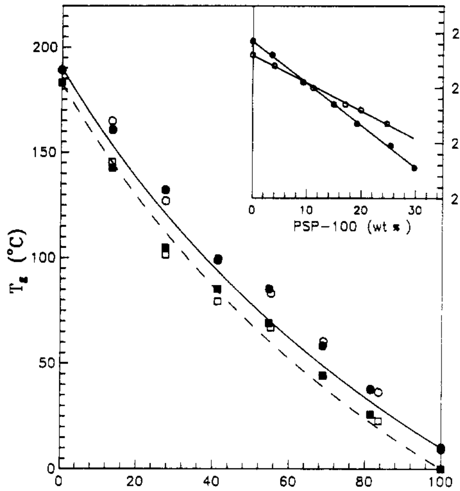


Figure 8. Glass transition temperature vs blend composition (see Figure 7): (●) T_g midpoint (at $\Delta C_p/2$); (■) T_g onset. The connecting curves were calculated according to eq 1. The window shows the corresponding melting temperature of CA45 and CA3 in these blends (T_m was taken at the tail end of the peak): (●) CA45; (○) CA3.

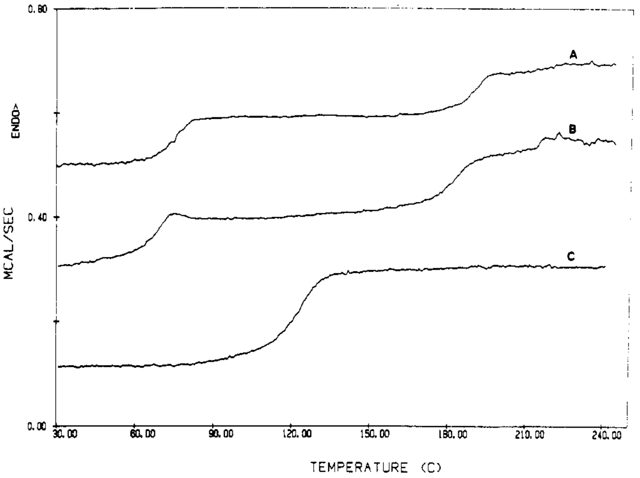


Figure 9. Differential scanning calorimetry traces of PSP/CA blends (1:1 by weight): (A) PSP-39; (B) PSP-32; (C) a rescan of B after annealing in the DSC cell at 200 °C for 100 min. The blends were cast films from *p*-dioxane.

The heat capacity change, ΔC_p, at T_g, for the wholly amorphous PSP-100/CA (Figure 10), as for most miscible organopolymer blends,[20,21] can be a combination of a weight fraction (W) expression

$$\Delta C_p = W_1 \Delta C_{p1} + W_2 \Delta C_{p2} \qquad (2)$$

where ΔC_{p1} and ΔC_{p2} are the heat capacity changes of the pure polymer components. Deviation from eq 2 is expected in semicrystalline blends, since the crystalline phase does not contribute to ΔC_p at T_g as indicated in Figure 6. If, indeed, the shift in the linear plot (Figure 10) is attributed to the crystalline fraction, then the degree of crystallinity estimated for the CA-rich blends is less than 8%.

The density measured for this series of blends decreases with the augmentation of the PSP fraction (Figure 11). It is generally expected that miscible pairs with strong intermolecular interactions will exhibit higher packing densities.[21] A slight increase in density over the value predicted from a weight-average density is found in the region of 30–70 wt % PSP. However, semicrystallinity and the inherent fact that miscibility in this system arises from interactions between pendant groups remotely situated to the polymer chains obscure the precise relationship between miscibility and density.

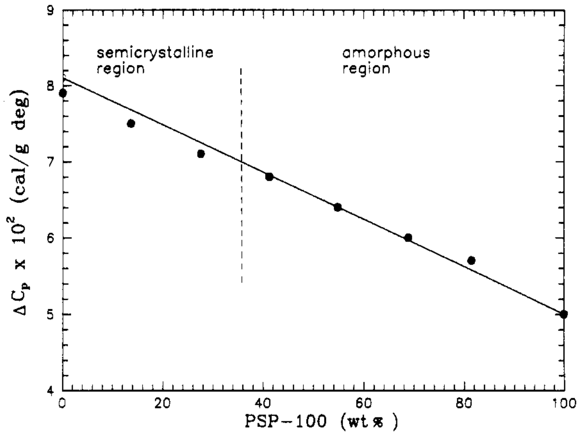


Figure 10. Heat capacity change (ΔC_p) vs PSP fraction, in a PSP-100/CA blend.

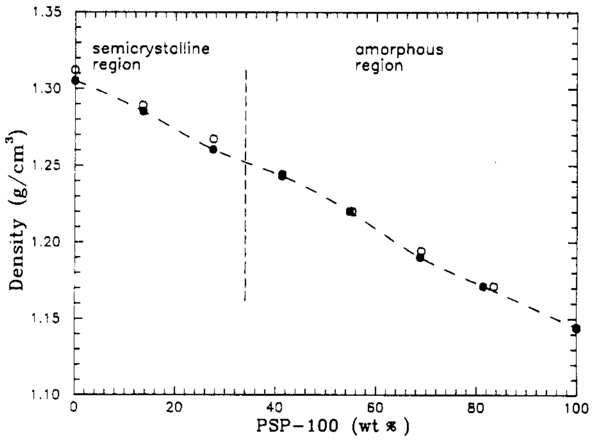


Figure 11. Density vs weight fraction of PSP, in PSP-100/CA blends: (●) CA45; (○) CA3.

Infrared Spectra Analysis. Some relevant data for this discussion concerning the degree of interaction as implied from infrared spectra are given here (a full account of the spectroscopic analysis will be reported in a subsequent manuscript[6]). The interaction between PSP and CA is clearly evident from the spectral shift of the phosphoryl band in Figure 12; the infrared absorption spectra of PSP-100 and PSP-32 are compared with the blended versions prepared from solution and without further annealing at a composition of PSP/CA 55:45 wt %. The phosphoryl (P→O) stretching band (1253 cm^{-1}) in the PSP-100/CA blend displays a significant downfield shift, ca. 10 cm^{-1}. In the blend with the partially phosphorylated version, PSP-32, which corresponds to thermogram B in Figure 9, the prominent peak does not shift; rather, a significant broadening of the phosphoryl absorption band in the downfield direction is clearly shown. Possible interference of the carbonyl ester band at ca. 1240 cm^{-1} was eliminated by spectrum subtraction.

The shifts of phosphoryl bands at the range of 10–13 cm^{-1} are comparable to those measured for trialkyl phosphates/water interactions, which were reported to correspond to a bond strength of 4–5 kcal/mol.[22-25] The interaction of CH_3OH with PSP-100, however, was reported to yield a much larger shift, >20 cm^{-1},[16] and was qualitatively assessed to have stronger interactions, ca. 8–10 kcal/mol. This is already comparable to the shift of 17 cm^{-1} found for the pair PSP-100/CA (10:90 wt %) in which most of the phosphoryl groups are locked in an interactive mode with the hydroxyl groups of the cellulose

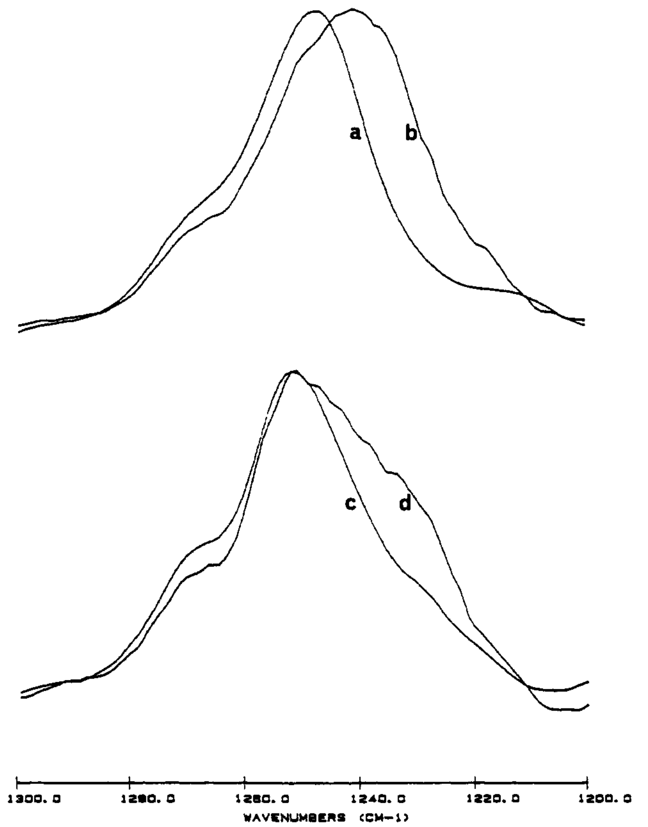


Figure 12. Infrared spectra of the phosphoryl (P═O) stretching band in a miscible (b) and a partially miscible blend (d). (a) PSP-100; (b) PSP-100/CA; (c) PSP-32; (d) PSP-32/CA. (The composition of PSP/CA is 55:45 by weight.)

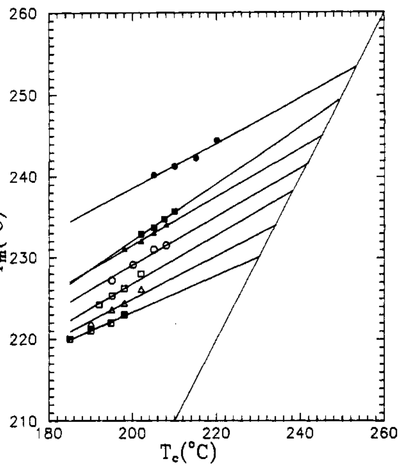


Figure 13. Hoffman–Weeks' plots of PSP-100/CA blends. Blend composition in volume % of PSP-100: (●) 0; (■) 4; (▲) 10; (○) 16.5; (□) 21; (△) 28; (▣) 32.5.

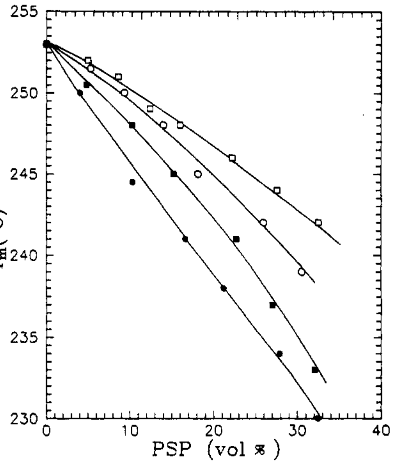


Figure 14. Melting temperatures of CA vs volume fraction of PSP in various miscible blends: (●) PSP-100; (■) PSP-95; (○) PSP-87; (□) PSP-60.

acetate. Since the cellulose acetate contains primary and secondary hydroxyls, its interaction modes with PSP are not uniform, as is suggested by the shape of the absorption band in Figure 12d. As mentioned above, these examples are given here merely as supporting data; an elaboration of the spectroscopic analysis is given in ref 6.

Melting Temperature Depression and Assessment of the Interaction Parameter. The DSC thermograms (Figure 8) reveal a definite melting temperature depression in the PSP-100/CA blends. This has been a common observation in blends of miscible semicrystalline polymers,[7-14] from which an interaction parameter can be extracted. The melting temperature depression in a blend consisting of miscible polymer pair A and B can be expressed by the equation[26]

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}= -\frac{RV_A}{\Delta H_f^\circ V_B}\left[\frac{\ln\phi_A}{N_A}+\left(\frac{1}{N_A}+\frac{1}{N_B}\right)\phi_B+\chi_{AB}\phi_B^{\,2}\right] \qquad (3)$$

where ΔH_f° is the heat of fusion of the pure crystallizable component A; ϕ_i and V_i are the volume fraction and the molar volume of component i, respectively; N_i is the degree of polymerization; R is the universal gas constant, T_m° and T_m are the melting temperatures of the pure crystallizable polymer and the blend, respectively; and χ_{AB} is the interaction parameter.

The interaction parameter χ_{AB} can be derived from eq 3 by using the equilibrium melting temperature for each blend composition. The values of equilibrium T_m were obtained from Hoffman–Weeks' plots, as was suggested before. Such plots were generated for PSP-100/CA blends and are shown in Figure 13. The measured values of T_m increase progressively with T_c. Reasonable linear extrapolation can be drawn up to the reference line $T_m = T_c$, yielding the extrapolated equilibrium melting temperature values. Similar plots were derived for four other blends consisting of PSP-95, PSP-87, PSP-60, and PSP-58. Plots of equilibrium T_m vs volume fraction for four sets of blends are delineated in Figure 14, revealing clearly that the rate of melting temperature depression depends largely on the degree of phosphorylation of the PSP.

In order to calculate interaction parameter values directly from eq 3, the magnitude of ΔH_f° (680 cal/mol of repeating unit) was extrapolated from Figure 6. Approximate molar volumes of the polymers were taken as the formula weight of a repeating unit divided by the densities. The calculated formula weights, the measured densities, and the molar volumes of polymers are presented in Table VI.

All the values of χ_{AB} obtained for the various blend compositions (Figure 15) are negative, indicating that the interactions between the two polymer components favor mixing. The considerably larger magnitude of χ for the blends with PSP-100, when compared to that with PSP-95, suggests that the distribution of phosphoryl groups between the meta and para positions, of the styrene ring, provides a better opportunity for interactions with the randomly distributed hydroxyl groups of the cellulose acetate.

Comparison between the interaction parameters obtained with the two different grades of cellulose acetate

Table VI
Parameters Used in Calculating the Interaction Parameters of Poly(styrenephosphonate diethyl esters) and Cellulose Acetate (30:70 vol %)

designation	density, g/cm^3	formula wt[a]	molar volume,[a] cm^3/mol	interaction param χ[b]
PSP-58	1.140	193	169	−0.10
PSP-60	1.141	196	171	−0.13
PSP-87	1.144	237	207	−0.22
PSP-95	1.147	247	215	−0.30
PSP-100[c]	1.144	254	222	−0.35
CA45	1.305	264	202	
CA3	1.312	266	203	

[a] Calculated from the molecular structures of polymers. [b] Calculated from eq 3 for PSP-CA (30:70 vol %). [c] Poly(vinylbenzylphosphonate diethyl ester).

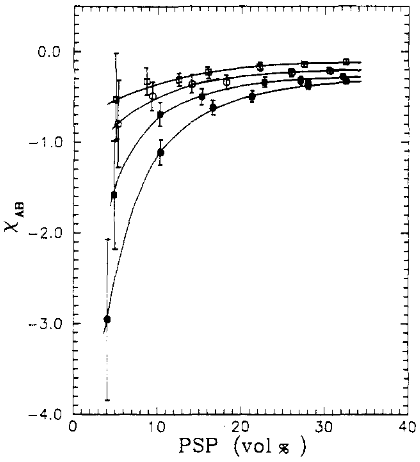


Figure 15. Interaction parameters, χ, of PSP/CA blends (as calculated from melting temperature depression) vs volume fraction of PSP: (●) PSP-100; (■) PSP-95; (○) PSP-87; (□) PSP-60.

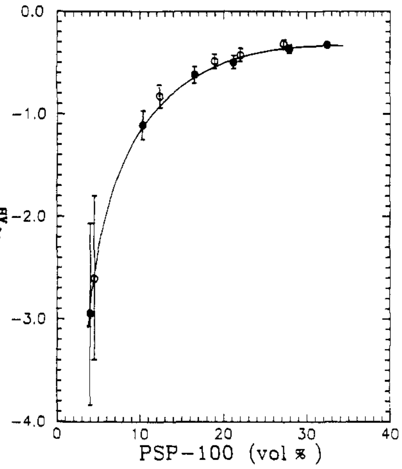


Figure 16. Interaction parameters of PSP-100 blended with CA vs volume fraction of PSP-100. (●) CA45; (○) CA3.

used with PSP-100 yielded nearly the same results (Figure 16). The data, as plotted, suggest somewhat higher interaction with CA45; this version contains larger fractions of hydroxyls totally, as well as that on the C(6) position (Table I).

The magnitudes of χ are comparable with those measured for other nonionic miscible polymer systems.[7-12] However, a strong composition dependency is suggested in Figures 15 and 16, with χ approaching asymptotic values for blends with progressively higher fractions of PSP. Such concentration dependency was also reported for other miscible pairs.[9,12] In the present case, the significant drop in χ shown for compositions having less than 15 (vol %) PSP, may also be attributed to the chemical nature and accessibility of the primary and secondary hydroxyl groups in CA. This is also in agreement with the spectroscopic results reported above that reveal a significant downfield shift in the phosphoryl stretching band, as the PSP fraction in the blend is decreased from 50 to 10 wt %.

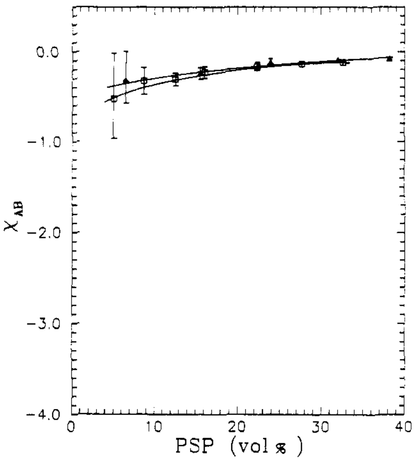


Figure 17. Interaction parameters of CA45 vs volume fraction of PSP: (□) PSP-60; (▲) PSP-58.

An attempt was made to determine the influence of residual chloromethyl groups on the miscibility by comparing the melting endotherms of PSP-58 with PSP-60 blends, the former contains ca. 12% chloromethyl moieties (chloromethylated polystyrene is immiscible with CA over the entire range of composition). The results shown in Figure 17 suggest only a marginal decrease in χ for the blends with PSP-58.

Conclusions

The experimental results of this study clearly show that poly(styrenephosphonate diethyl ester) is miscible at the entire composition range with cellulose acetate. Partly phosphorylated PSP grades, which are in fact random copolymers, of styrene/styrenephosphonate ester, having at least one phosphoryl group per two styrene units, are miscible with CA when prepared from mutual solvent or from melt. Blends with PSP grades having a lower content of $P \rightarrow O$ groups, which would not form homogeneous blends from a common solvent with CA, should be prepared from the melt or by annealing the heterogeneous solid blends at temperatures above T_g(CA) (Figure 4 and refs 3 and 4). While grades of PSP having as low as one phosphoryl ester per four styrene units do mix spontaneously with CA at temperatures $\geq T_m$, the content of phosphoryl ester required for miscibility may be even lower. Thermal analysis of this aspect, however, becomes progressively difficult as the degree of T_m depression decreases. Cellulose acetate thermally degrades near its melting temperature, and annealing PSP/CA heterogeneous grade containing phosphoryl-poor PSP for the required time to complete mixing may involve a thermal degradation factor at high T_m.[3] Since it has been categorically proven recently that phosphorylated polymer interactions with species containing a hydroxyl group yield LCST type phase diagrams,[27] it is tentatively concluded here that the PSP/CA phase boundary is above the degradation temperature of CA.

In many respects, the blends of PSP/CA reported herein follow the general behavior observed for most known semicrystalline miscible pairs. Thus, crystallization of CA appeared to be almost completely impeded when the fraction of PSP is more than ca. 30%; the melting temperature of cellulose acetate exhibits progressive depression with increasing PSP fraction; T_m depression is clearly dependent on the degree of phosphorylation and so is χ. The interaction parameter is strongly dependent on the composition of blends as well, suggesting various levels of interactions with CA. This aspect has to be further clarified in spectroscopic studies.

It should be emphasized, in this concluding section, that $\Delta H_f°$ used in calculating χ is an extrapolated number (Figure 6); therefore, the absolute values of χ may differ some from what is quoted in this paper. For example, a reported $\Delta H_f°$ value for cellulose triacetate, CTA (2360 cal/mol),[28] is much higher than the values for CA quoted in this work. The crystalline diffraction pattern of CTA resembles,[5] with slight deviation in d-spacing, that of CA (Figure 3). However, it is unlikely that the crystalline structure of the CA grade used in this work is made of wholly CTA blocks (T_m > 300 °C). Therefore, the crystalline domains of CA can be described rather as a "defective" CTA structure, accounting for the lower T_m and $\Delta H_f°$. The possibility that CA grades would have higher $\Delta H_f°$ than that extrapolated from Figure 6 is not implausible, and further work is being conducted in this laboratory concerning this aspect. High-resolution FT-IR proved to be very sensitive to these types of blends, and efforts are currently under way to obtain more detailed information concerning the nature and strength of the bonding between the phosphoryl and hydroxyl groups. This, as well as data from transmission electron microscopy studies, will be reported in a subsequent paper.[6]

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