On the compatibility and thermally induced blending of poly(styrene phosphonate diethyl ester) with cellulose acetate

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The miscibility of poly(styrene phosphonate diethyl ester) (PSP) with cellulose acetate (CA) was studied. Experiments were designed to prove that these polymers are a miscible pair. The study revealed that when blends were prepared from a solution with partially phosphorylated polystyrene, favourable conditions for crystallization of the cellulose acetate prevailed. Upon conversion of the crystalline regions into amorphous domains—as done by heating the sample in a differential scanning calorimeter—an amorphous homogeneous blend spontaneously formed. The merger of the CA- and PSP-rich phases in the temperature range 190–200°C (slightly above T_g of CA) was recorded to yield the plot of the corresponding changes in the glass transition temperature vs. time. Computation of the corresponding values for the changes in specific heats clearly indicated the exchange of matter between the two merging phases. However, it also showed that prolonged exposure of the sample to this temperature results in chemical changes (i.e. degradation and crosslinking) in the CA-rich phase. The results of this study revealed that PSP is miscible with CA at a lower degree of phosphorylation than previously thought; thus, one phosphoryl ester per six styrene units in PSP will still render this polymer miscible with cellulose acetate.

(Keywords: polymers blends; polymer miscibility; glass transition; poly(styrene phosphonate); cellulose acetate)

INTRODUCTION

The compatibility of cellulose acetate with aromatic polymers that contain phosphoryl ester pendant groups[1-3] or pyridine groups[4,5] has previously been reported. Cellulose acetate was reported to be miscible in all proportions with such polymers. Apparently, hydrogen bonds formed between the cellulose acetate (which contains approximately one hydroxyl group per two glucose units) and the electron-rich phosphoryl and pyridine groups.

In all previous work[1-5] the polyblends were prepared from solution. The polymers were dissolved in a common solvent to yield a homogeneous transparent solution. Upon removal of the solvent, a transparent amorphous or semicrystalline polyblend displaying one glass transition temperature was produced. High-resolution transmission electron microscopy studies revealed complete miscibility of these polymers[5]. In all the cases where the blends contained more than 30 wt% of cellulose acetate, a fraction of this polymer crystallizes to yield semicrystalline polyblends.

Conventional thermal blending of these polymers without solvent was considered unattainable due to the fact that the glass transition and melting temperatures of cellulose acetate are too high (≈185°C and ≈225°C, respectively) and thus too close to the polymer's thermal degradation temperature (250°C). Also, it was shown that the miscible blends of poly(2-vinylpyridine) (P2VPy) or poly(4-vinylpyridine) with cellulose acetate decompose into two phases within this temperature range. The phase separation was evidenced by the disappearance of the single T_g of the miscible pair, and the appearance of the separate T_g values of the parent polymers[5]. Thus, for example, phase separation of the miscible blend P2VPy/CA (1:1 wt%) occurred at 200°C. Although this may indicate that a lower critical solution temperature (*LCST*) exists for this polymer pair, it is by no means certain, because thermal blending of this polymer pair without solvent is not possible and the removal of solvent 'locks' the pair into a glassy state.

Since the miscibility of these polymer systems is primarily due to specific interactions, the need to have a solvent to achieve homogeneous blends renders the interpretation of the blending results difficult. This is especially true in the present examples, where solubility in the pertinent solvents is due to polar and hydrogen bonding interactions. In such cases the solvent molecules may often form bridges between different polymers, as in the events where steric parameters do not favour the otherwise possible site-to-site interaction between the polymer pair.

The objective of this work is to provide proof that cellulose acetate is thermodynamically compatible with the type of polymers mentioned above. Considering all the constraints, poly(styrene phosphonate ester) blends were selected for this task. The compatibility of cellulose acetate with phosphorylated polystyrene depends largely on the degree of phosphorylation. A decrease in the content of phosphoryl ester groups leads progressively to a lower miscibility[1-3]. A miscible blend that displays one glass transition temperature is produced when a fully phosphorylated polystyrene (i.e. one phosphoryl ester per polymer unit) is blended with cellulose acetate using a

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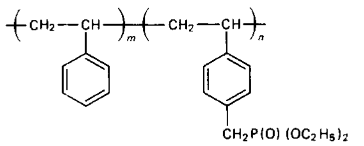
common solvent. Unlike the blends with poly(vinylpyridines), this blend does not decompose into two phases below the thermal decomposition temperature of cellulose acetate. Therefore, it was considered a good candidate for a study of the thermal blending of non-homogeneous mixtures composed of poly(styrene phosphonate ester) and cellulose acetate. Such mixtures, however, should be intimately blended before thermal blending is attempted, because the high blending temperatures that are required (> 190°C) can be applied only for a relatively short period of time. Longer heating causes degradation and crosslinking reactions, which hamper spontaneous exchange of material between the two polymer phases. Accordingly, the polymer blends were prepared from partially phosphorylated polystyrene and cellulose acetate mixed in a common solvent, and upon casting yielded transparent films which exhibited microphase separation. Samples of these blends were subsequently annealed at elevated temperatures to produce homogeneous blends.

EXPERIMENTAL

Materials

The cellulose acetate used (designated CA 394-45) was a product of Tennessee Eastman, and had a molecular weight $M_w = 62\,000$, acetyl content 39% and $T_g = 190$°C.

Three samples of poly(styrene phosphonate diethyl ester) (designated PSP) were used. The general molecular formula of PSP is:



The phosphorylation of the polystyrene is a random substitution, where *n* and *m* are used only to express the degree of substitution. The partially phosphorylated polymers were synthesized from polystyrene as previously described[1]. The number-average molecular weight $\bar{M}_n$ of these polymers was determined by membrane osmometry. The three PSP samples used in this study had the following characteristics.

(i) PSP_1: $\bar{M}_n = 230\,000$, $T_g = 79$°C, $m/n = 2.6$ (note that degree of phosphorylation is expressed as m/n ratio, see molecular formula);

(ii) PSP_2: $\bar{M}_n = 118\,000$, $T_g = 75$°C, $m/n = 3.0$;

(iii) PSP_3: $\bar{M}_n = 28\,000$, $T_g = 56$°C, $m/n = 5.5$.

(PSP_1 was prepared from a monodispersed polystyrene with $M_w = 217\,000$).

Solvent: *p*-dioxane, Fisher, Inc., 'Purified' grade The solvent was redistilled and stored over molecular sieves before use.

Sample preparation

Three samples composed of cellulose acetate blended with PSP_1, PSP_2 and PSP_3 were prepared by separately dissolving each polymer in dioxane to produce 5–10 wt% solutions. The solutions were then mixed to provide a compositional ratio of CA/PSP (1:1 wt%). The transparent homogeneous ternary mixtures were subsequently cast onto glass plates using a casting blade with 350 μm clearance. The cast layers were allowed to dry slowly for 2 h in a chamber containing dioxane vapour. The chamber was then evacuated for 24 h at 30 mmHg. Subsequently, the film samples were placed in a vacuum oven at 45°C for 3 days, or until no residual dioxane was detectable in the films when tested in infrared spectroscopy.

Differential scanning calorimetry measurements

Film samples of PSP/CA (5–10 mg) were annealed and tested in a Perkin–Elmer DSC-4 equipped with a microprocessor control. Scanning rates of 20°C min^{-1} were used for all scans. To prevent oxidation, both the measurements and annealing were conducted under a steady flow of dry nitrogen. The values of the glass transition temperatures, T_g, were taken at the half-point of the heat capacity change, ΔC_p, during the transition (see *Figure 1*). The change in ΔC_p at T_g was calculated from the vertical distance between the two extrapolated baselines at T_g. The width of the glass transition region, ΔT_g, was defined as the region confined between the lower and upper intersections of the extrapolated baselines and the tangent to the inflection point at T_g, as shown in *Figure 1*.

A sequence of d.s.c. thermograms is shown in *Figures 1–3*. The first thermograms shown in *Figures 1* and *3* were the runs of the 'as-cast' samples. These samples were quench-cooled at a rate of 50°C min^{-1} immediately at the termination of each heating cycle. Prolonged annealing was not employed with these two samples. The sequence of thermograms shown in *Figure 2* does not include the first run on the as-cast sample. The first heating cycle of this sample produced a similar thermogram to the one shown in *Figure 1*, trace A. (The thermogram was omitted from *Figure 2* because the large endotherm around 70–100°C would not fit into the figure.)

RESULTS AND DISCUSSION

Although 1,4-dioxane is a relatively good solvent for each of the polymers, the transparent PSP/CA blends that were prepared are not completely miscible—as judged by the d.s.c. thermogram of the as-cast PSP/CA, i.e. scans A in *Figures 1–3*. All three samples show at least two amorphous and one crystalline phases. The as-cast PSP/CA sample, shown in *Figure 1*, scan A, displays a rather large crystalline melting endotherm between 215 and 230°C. Following a fast quenching from the melt, a re-run, shown in the second thermogram (*Figure 1*, trace B), reveals the existence of two amorphous phases: a PSP-rich phase with a transition at 90–110°C, and a CA-rich phase with a transition at 170–190°C. A trace of crystalline melting point also appears at 208°C. The same is shown in *Figure 2*, scan A, where only partial mixing has occurred as is indicated by the presence of two separate glass transitions (shifted slightly towards each other) at 78°C and 170°C. The CA exhibits a small crystalline melt transition at 208°C. It should be mentioned that pure CA, when cast from solvent, exhibits T_m of 225 ± 2°C, as is the location of the T_m trace shown in *Figure 3*.

The endotherm at 208°C was found to be highly reproducible and it is believed to belong to trace cellulose acetate crystals whose structure has yet to be identified.

Heating the sample above T_m allows thermal mixing to prevail as shown in the subsequent thermograms in *Figures 1–3*.

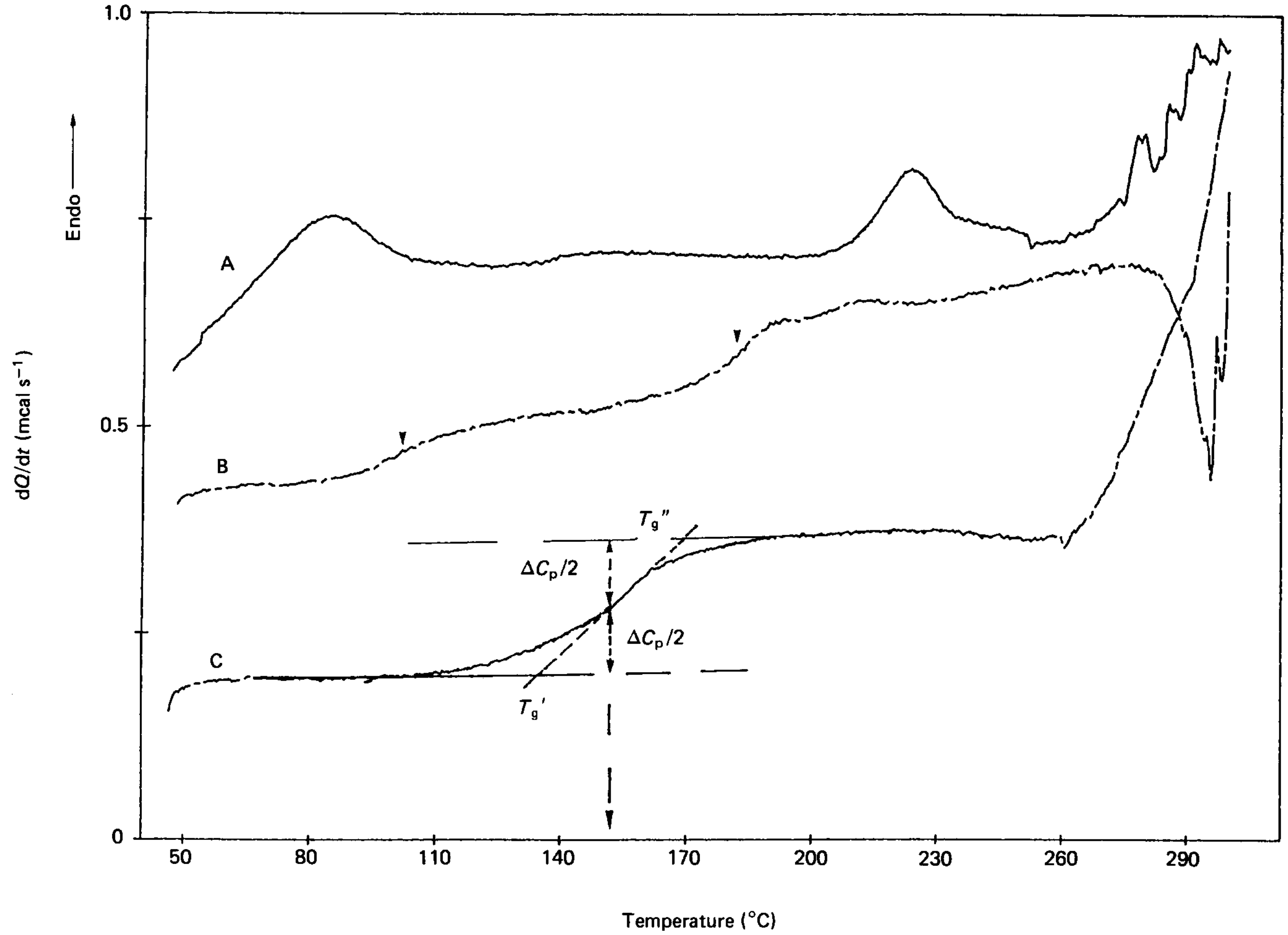


Figure 1 Differential scanning calorimetry thermograms of cellulose acetate/poly(styrene phosphonate diethyl ester)—CA/PSP$_1$. Shown are three consecutive thermograms: A, as-cast; B, after one melt-cool cycle 40–229°C; C, after two melt-cool cycles

The merger of the T_g values was systematically studied by applying a sequence of thermal treatments, shown in *Figure 2*, for a PSP$_2$/CA sample. In this set of experiments the sample was annealed in the d.s.c. for 16 h. The first thermogram (*Figure 2*, scan A) shows a crystalline trace at 208°C. The second thermogram (*Figure 2*, scan B) indicates that this crystalline region did not recover following the heat-quench cycle. Subsequently, the annealing temperatures were kept 20°C higher than the T_g values of the CA-rich phase, which in turn resulted in spontaneous mixing of the polymer components.

Figures 1 and *2* clearly show the progressive merger of the T_g values. *Figure 2* also shows that ΔT_g for both phases does not spread significantly as exchange of materials between the phases takes place. In addition, the heat capacity changes, ΔC_p, associated with the T_g (shown in *Table 1*) clearly reflect an exchange of material between the two phases. The ΔC_{p1} (of the PSP-rich phase) increases asymptotically to a level that is very close to the mean value computed for the combined material, i.e. 0.058 cal g^{-1} °C^{-1}. The progressive decrease in ΔC_{p2}, shown in *Table 1* for the CA-rich phase, is far more dramatic than the compositional changes of this phase, as deduced from the corresponding blend's T_g values (using either Gordon–Taylor or Fox expressions). The final measurable value of ΔC_{p2} (*Figure 2*, scan D) decreased below that of ΔC_{p1}, indicating that, concurrent with the thermal mixing with the PSP, the CA-rich phase is experiencing some thermal degradation and crosslinking due to the extended annealing process. This was further evidenced by the total collapse of ΔC_p after 16 h of annealing as shown in *Figure 2*, scan F. Note also that the cumulative ΔC_p (*Table 1*) is reduced from 0.105 in the first thermogram (*Figure 2*, scan A) to 0.087 cal g^{-1} °C^{-1} for *Figure 2*, scan D. It should be emphasized that in computing the ΔC_p values we initially assumed an equal distribution of material between the two phases—as the blend is composed of PSP/CA in a 1:1 weight ratio and the ΔC_p value computed for the blend shown in *Figure 1*, scan C, is a mean value of the polymer components. However, the correct distribution between the phases is not known and, therefore, the ΔC_p values quoted in *Table 1* should be considered with caution. Evidence for some thermal decomposition in the film was also given by the dark brown colouration of the samples that were annealed below T_m for such prolonged periods of time. (Note, however, that instant decomposition prevails above 250°C as is shown in all three thermograms in *Figure 1*.) Pure CA, when exposed to such a prolonged annealing condition, produced an insoluble, dark carbon powder. Unlike the CA, the PSP-rich phase is not as susceptible to thermal decomposition. The PSP does not decompose in this temperature range, and was shown previously[1] to remain unaffected at temperatures above 300°C.

The results shown above definitely suggest that PSP

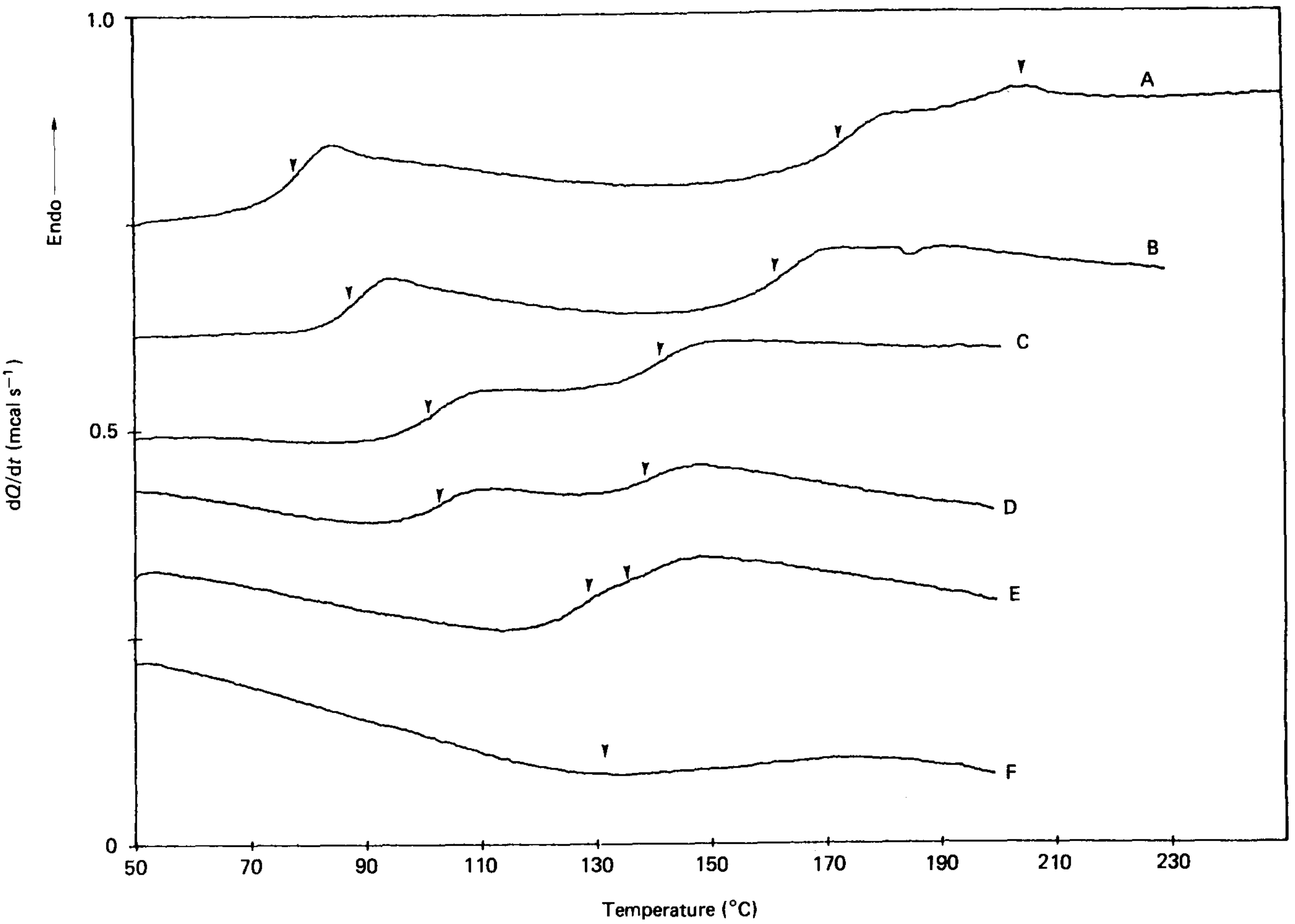


Figure 2 Differential scanning calorimetry thermograms of cellulose acetate/poly(styrene phosphonate diethyl ester)—CA/PSP$_2$. Thermograms A and B are the produces of two consecutive heating cycles that proceeded after the first heat cycle, of the as-cast sample, which is not included in the figure. The rest of the thermograms were consecutively run as rollows: C, after 10 min at 200°C; D, after 20 min at 200°C; E, after 3 h at 190°C; F, after 16 h at 190°C (note, the sample charred slightly)

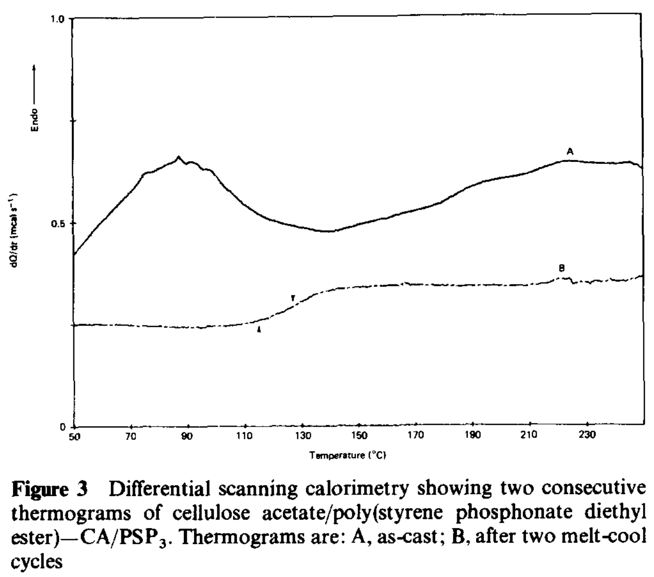


Figure 3 Differential scanning calorimetry showing two consecutive thermograms of cellulose acetate/poly(styrene phosphonate diethyl ester)—CA/PSP$_3$. Thermograms are: A, as-cast; B, after two melt-cool cycles

and CA are a miscible pair. The partial miscibility that these blends display when prepared from solution is primarily due to the favourable conditions for crystallization of the cellulose acetate. Thus, the slow evaporation of the solvent that was used in the preparation of these blends results in a semicrystalline polyblend rather than an inherently incompatible mixture. Upon conversion of the crystalline regions into amorphous domains (as was done by heating the samples above T_m), an amorphous, homogeneous blend is spontaneously formed. Therefore, although thermal blending clearly prevails and the blending rate is enhanced by elevation of the temperature, there is still no reason to conclude that this polymer pair exhibits an upper critical solution temperature (*UCST*) behaviour. Rather, this system is believed to have a hypothetical phase boundary somewhere above the decomposition temperature of the blend (while apparently in the case of the poly(2-vinylpyridine) mentioned above the phase boundary is located between T_g and T_m). It is important to note that the extended annealing period—above T_g but below T_m—shown in *Figure 2* does not reproduce crystallinity in the sample; pure CA as well as other semicrystalline polymers do recrystallize under similar annealing conditions. Some important qualitative observations should be pointed out. The PSPs used in this study represent a wide range of molecular weights. This fact, however, did not affect the final outcome; all three samples ended up exhibiting one T_g, as was expected, and PSP$_3$ with the lowest M_n seems to blend at faster rates. The differences between the PSP samples, however, do seem to affect the crystallization of the cellulose acetate when cast from solution. In this regard

Table 1 Glass transitions and heat capacity changes in thermally induced blending of CA/PSP_2 (shown in *Figure 2*)

	PSP-rich phase			CA-rich phase		
Scan	T_{g1} (°C)	ΔT_{g1} (°C)	ΔC_{p1} (cal g^{-1} $°C^{-1}$)	T_{g2} (°C)	ΔT_{g2} (°C)	ΔC_{p2} (cal g^{-1} $°C^{-1}$)
–[a]	(74.8)	(12±2)	(0.035±0.005)	(190)	(9)	(0.081±0.005)
A	77	9±2	0.0480±0.005	170	21±2	0.57±0.005
B	87	12±2	0.0485±0.01	160	17±2	0.049±0.005
C	99	15±2	0.0485±0.01	143	18±2	0.042±0.005
D	105	14±2	0.0530±0.01	141	14	0.037±0.008
E	127	19	0.0530±0.01	130	–	–

[a] Values for the homopolymers

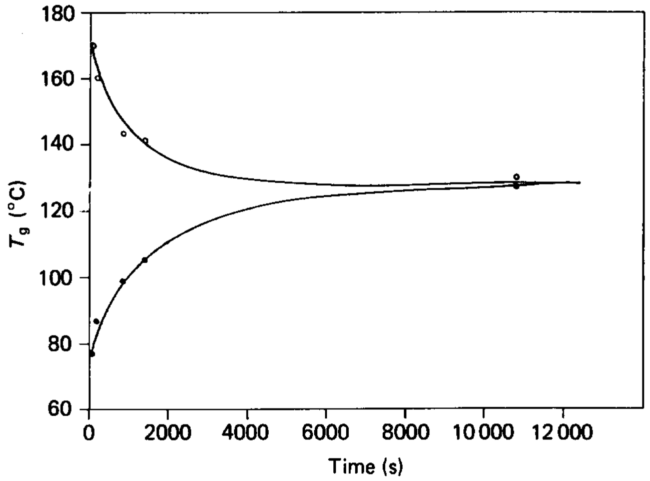


Figure 4 Glass transitions vs. time of cellulose acetate and poly(styrene phosphonate diethyl ester), CA/PSP_2 blend, as recorded during the process of thermal blending at 190–200°C: ○, CA; ●, PSP

PSP_1 seems to induce more crystallinity in the CA than PSP_3. The fact that a full conversion into the amorphous state is achieved in the former, while the CA/PSP_3 blend maintains some residual crystallinity with T_m of 225°C (*Figure 3*), may suggest that the crystallites are smaller in CA/PSP_1. One of the most important outcomes of this study is that PSP is compatible with CA at a lower degree of phosphorylation than previously thought. The critical degree of phosphorylation that is necessary for miscibility with CA has yet to be determined.

The thermal blending reported in this article provides a direct and relatively simple way to obtain information about the mobility of the polymer components. A plot of T_g vs. time represents the continuing change in the composition of the phases as thermal blending progresses (*Figure 4*). The curve patterns resemble, to a large extent, absorption behaviour into a polymer network[6]. A mathematical model from which the diffusion coefficient of the macromolecules could be calculated from such curves is being developed in this laboratory. Preliminary calculations based on Fickian diffusion[7] indicate a diffusion coefficient of 10^{-12}–10^{-13} cm^2 s^{-1} in a temperature range of 190–200°C, assuming a constant diffusion coefficient and domain diameter of 10^3–10^4 Å (the latter shown by transmission electron microscopy). The full mass-transport analysis concerning the prevailing exchange between the phases will soon be reported from this laboratory[8].

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