

Poly(ethylene Terephthalate)/Cellulose Blends

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Synopsis

Amorphous poly(ethylene terephthalate) (PET) and cellulose blends in film form were obtained by room temperature hydrolysis of PET/cellulose trifluoroacetate solution cast films. Evidence is presented indicating that the cellulose, or the water associated with it, nucleates the crystallization of the PET during differential scanning calorimetry (DSC) runs. At about the 50/50 composition, a phase inversion, from continuous PET to continuous cellulose appears. Hydrolysis and/or annealing in water at the boil yields a mixture of cellulose II and cellulose IV. The nature of the cellulose appears to be different in the case of the room temperature hydrolyzed structures. Hydrolysis appears to proceed more readily when the films are richer in the cellulose component.

INTRODUCTION

The previous paper¹ described the preparation of clear films of blends of PET and cellulose. The route to these involved first dissolving cellulose and PET in a common solvent, a mixture of trifluoroacetic acid (TFA) and methylene chloride. Cellulose and its derivatives had been earlier studied for their cholesteric liquid crystalline properties in such mixtures.^{2,3}

The IR analysis of the films obtained from solution casting of the blends clearly demonstrated that the blends were not with cellulose per se but rather with the partial trifluoroacetate esters of cellulose.^{1,4} Infrared spectra and DSC measurements indicated specific polymer-polymer interaction, although two glass transition temperatures were observed. Hydrolysis of the blend films was accomplished by suspension in water at the boil for 2 h. The resulting clear films were blends of semicrystalline PET and a mixture of cellulose II and IV polymorphs. No specific polymer-polymer interactions were apparent.

In this study, films were prepared by hydrolysis at room temperature, as well as in boiling water, of the TFA/methylene chloride solution cast films. This permitted a comparison of the precrystallized to the annealed postcrystallized PET/cellulose blends.

EXPERIMENTAL

The prehydrolyzed films used in this study were those described in the previous paper¹ and were prepared from the same sources, Whatman cellulose and Goodyear PET with a reported intrinsic viscosity of 0.59. The solvent was a mixture of distilled TFA and methylene chloride in a ratio of 70/30 by volume, and the concentration of polymer was 5% weight on volume. The solutions were cast on a glass plate and rapidly flash dried

using a hot air gun to prevent condensation of moisture, the procedure requiring no more than 1 min. The glass plates were placed in a vacuum oven at 50°C for about 30 min under full mechanical pump vacuum, removed, and the films carefully separated from the glass plates. Drying was conducted for a week at 50°C under full vacuum. The films were exposed to ambient conditions under varying high relative humidities for a period of 4 months. Infrared analysis showed them to be essentially converted into blends of cellulose and PET. The IR absorption spectra indicated the presence of trace levels of trifluoroacetate ester among the PET-rich fractions. All the films were suspended in water at room temperature (RT) for 2 weeks. Little change in the infrared spectra was evident in the resulting films after drying.

Films were also suspended in water at the boil for 8 h. The IR spectra showed complete conversion to cellulose with no trace of trifluoroacetate band present. Both room temperature hydrolyzed and boiling-water-treated films were dried at 50°C under vacuum for 1 week and maintained in envelopes under ambient conditions.

The DSC scans were run with a DuPont 1090 instrument on 10–15 mg size samples under a nitrogen stream at 5 cc flow per minute. Infrared spectra were determined using a Nicolet 6000 Fourier Transform Infrared (FTIR) spectrometer. X-ray spectra were obtained using a Philips XR6-3000 goniometer equipped with vertical diffractometer and scintillation detector and employing nickel-filtered copper radiation.

RESULTS AND DISCUSSION

A number of features are apparent from the DSC curves for the RT-hydrolyzed films (Fig. 1). The curves are composites of (in ascending temperatures) a typical amorphous type PET T_g , a PET crystallization exotherm, an endotherm associated with the water bound to the cellulose, and the PET melting endotherm. The corrected and PET normalized temperature and energy data are shown in Table I. Most interesting is the observation that the peak temperature of the crystallization exotherm decreases as the cellulose content increases. Such a depression of the PET crystallization temperature by a second blend component during the DSC heating regime has been reported by Kimura et al.⁵ In the latter study, blends of PET and a polyarylate based on bisphenol-A, tere- and isophthalic acids were melt-cast into films which were immediately quenched. The authors interpreted their observed crystallization temperature depression as an indication of an unspecified interaction between the PET and the polyarylate. It should be noted that, like our system, the second component is not thermodynamically compatible with the PET.

Our interpretation of the depression of the crystallization temperature is that the cellulose or the water associated with the cellulose (or perhaps an impurity) nucleated the crystallization of the PET. It is interesting that the crystallization onset temperature, which is also depressed, is lowered to close to the boiling point of water. In another study on PET crystallization, Aharoni⁶ found evidence that water released from a hydrated alu-

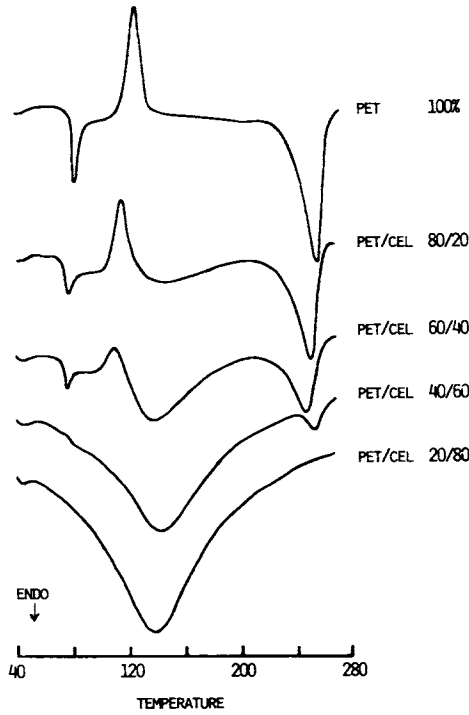


Fig. 1. DSC curves for RT hydrolyzed PET/cellulose films.

mina could act, under certain circumstances, as a nucleant for PET crystallization.

It should also be noted that at around the 50/50 composition, the exotherm is no longer visible. As can be deduced from Figure 1, this can be accounted for partially by subtracting the water endotherm from the crystallization exotherm. The curves for the compositions, increasing in cellulose to approximately the 50/50 level, show from the skewed symmetries of the water endotherms that such a subtraction is operating. At compositions richer in cellulose, the curves change in nature. The water endo-

TABLE I
Room Temperature Hydrolyzed PET/cellulose Films

Composition	Crystallization peak (°C)	Crystallization heat ^a (J/g)	T_m (°C)	Melting heat ^a (J/g)
100/0 PET/cell	125	23	254	49
90/10	122	22	251	48
80/20	116	19	251	52
70/30	115	15	253	45
60/40	110	10	248	48
50/50	111	2	246	32
40/60	—	—	254	11
30/70	—	—	253	2

^a Corrected for PET content.

therms are much more symmetrical, as if there was little if any crystallization exotherm to perturb the endotherm. Moreover, the appearance of the PET T_g changes markedly, becoming much less prominent. Interestingly, the DSC curves for the PET/polyarylate blends,⁵ despite the absence of the water complication, show similar changes at around the 50/50 composition. We believe these changes to be associated with phase inversion. At compositions greater than 50% in PET, the continuous phase is PET and the cellulose is dispersed therein. At compositions richer in cellulose the situation is reversed.

Curiously, all of the above behavior, i.e., the depression of the crystallization temperature, the diminishing of the exotherm and the marked change in the T_g appear, at least qualitatively, in the DSC behavior of amorphous melt cast neat PET,⁷ which has been annealed for different lengths of time at a given temperature. One observes the similar behavior as a function of annealing time instead of as a function of increasing second component. Annealing involves increasing degrees of induced crystallization prior to DSC scanning. From the IR spectra the two-component system does not. If one assumes that, in the former, the crystals formed over a given annealing time act as nuclei for crystallization during the DSC scan, then at least the crystallization temperature depression resemblance can be accounted for.

The enthalpy of the melting point is relatively constant up to about the 50/50 composition and then drops off rapidly. This is considered to be supporting evidence that phase inversion occurs at around this composition. Either the finely dispersed PET particle do not crystallize and therefore do not melt or they are so small that surface to volume considerations dictate a very much lower enthalpy of melting.

The observed enthalpy of crystallization of the neat PET film is substantially less than the observed enthalpy of melting. This phenomenon has been reported for amorphous PET previously.^{7,8} In our case, the ratio of exotherm to endotherm is about 45%. Proposed explanations for this phenomenon include continuous melting and recrystallization up to the observed melting point.⁷ This explanation for our data requires a significant amount of "hidden" exotherm to balance out the enthalpies. However, no other explanation is apparent. This will be discussed again below.

Figure 2 shows DSC curves for films which were suspended in boiling water for 8 h. No crystallization peak is apparent, and the T_g appears to have lost its prominence. The only unusual feature is the rather well-defined low-temperature endotherm in the case of the neat PET and the 90/10 composition (Fig. 3). Two interpretations are possible to account for this. One is that the peak is the result of evaporation of water. If this is correct, then there must be two kinds of water; witness the beginning of the appearance of a second peak in the 90/10 case. The problem with this explanation is that the peak in the case of the 100% PET is at a higher temperature than the new peak in the 90/10 composition. Water associated with PET should be much less bound than that associated with cellulose. Therefore, the temperatures of the peaks are in the wrong order.

A more reasonable interpretation is that the low-temperature endotherm visible in the boiled neat PET and 90/10 curves is associated with the

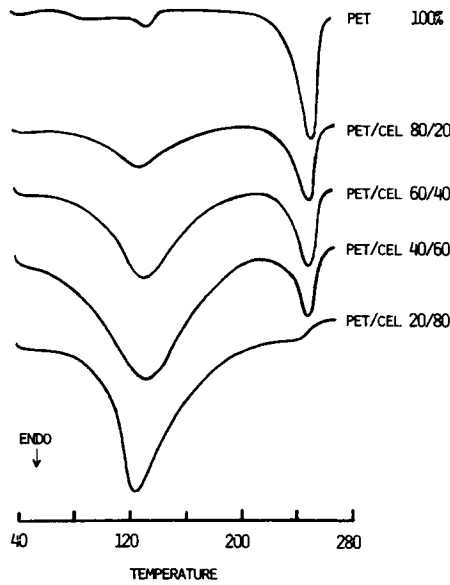


Fig. 2. DSC curves for boiling water hydrolyzed PET/cellulose films.

melting of imperfect PET crystals. The work of Lin and Koenig⁷ presents a set of DSC curves as a function of annealing time of amorphous PET. The longer the annealing time, the smaller the DSC crystallization exotherm. At greater than a critical time, characteristic of the annealing temperature, a melting endotherm becomes apparent. This melting is of imperfect crystals formed during the annealing. Presumably, we are seeing the same phenomenon in the 8-h boiled films.

The infrared spectra of the RT and boiling-water-hydrolyzed films were compared. For every composition other than the pure cellulose film, the peaks assigned to the *trans* glycol conformations were strongly enhanced by the boiling water. Concurrently, the *gauche* conformation peaks were diminished. Peak assignments were from various papers by Koenig.^{7,9-11} Examples of some of the changes are shown in Figure 4 for the neat PET

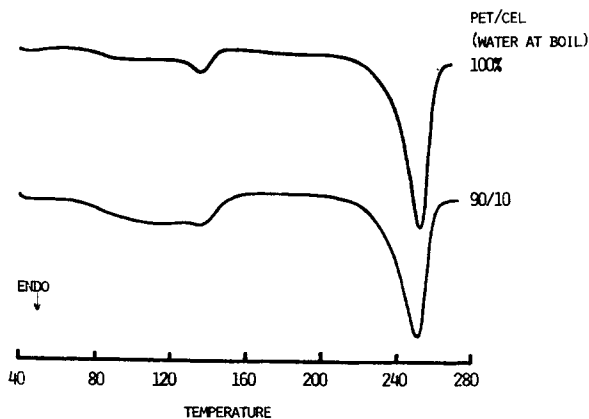


Fig. 3. Boiling-water-treated films—low temperature endotherms.

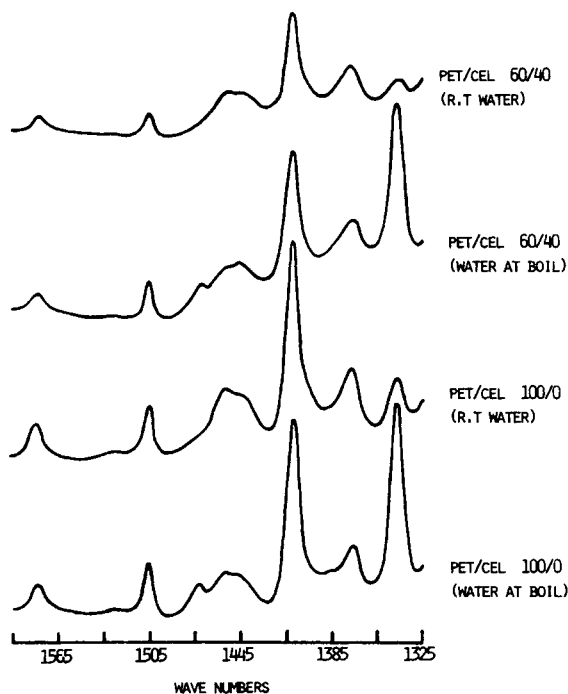


Fig. 4. IR spectra for RT and boiling-water-hydrolyzed films.

and 60/40 PET/cellulose films. The most obvious peak changes are at 1342 (*trans*), 1472 (*trans*), and 1372 cm^{-1} (*gauche*).

Estimates of the percent crystallinities of the PET films were calculated from the $973 \text{ cm}^{-1}/1579 \text{ cm}^{-1}$ ratio using the X-ray/IR correlations of Aharoni.¹² The RT-hydrolyzed PET was found to be amorphous while the boiled film had 24% crystallinity. The former result confirms that the technique for casting films and the room temperature hydrolysis are mild enough treatments to avoid crystallization of the PET.

The value for the crystallinity of the boiled sample is of interest when compared against the DSC high temperature melting endotherm of 47 J/g. The latter divided by the enthalpy of fusion of PET should yield the percent crystallinity just before melting. The enthalpy for PET is somewhat controversial with values covering a range from about 115 to approximately 136 J/g, the latter determined by Starkweather et al.¹³ employing the Clausius-Clapeyron equation. Using this range, the value for the crystallinity just before melting was approximately 35–41%. This means that the DSC curve for the boiled PET film had hidden within it the exotherm corresponding to the missing 11–17 J/g (actually somewhat more, considering the small low temperature endotherm evident in Fig. 2). Presumably this "exotherm" represents a combination of crystallization and perfection of crystals over the scan from about 100°C to the melting point. This explanation is, of course, similar to that above for the RT-hydrolyzed sample except that about 45% of the final endotherm is accounted for in the measured DSC crystallization exotherm above.

The cellulose IR absorbance peaks show small but distinct changes between the RT and boiling-water-treated films. Absorbances are enhanced in the latter case at 1280, 1335, and 1442 cm^{-1} (Fig. 5). Also the region between 3320 and 3480 cm^{-1} characteristically becomes more detailed and looks more like a mixture of cellulose II and IV polymorphs (Fig. 6) reported earlier.¹ The X-ray goniometer traces on the RT films differ from the corresponding boiled samples in terms of both components. The PET results are what is expected, that is, an amorphous pattern for the RT and a semicrystalline pattern for the boiling water case. However, the boiled water patterns, though nonuniform from sample to sample, were quite different for the cellulose-rich films. From the reflections at 2θ angles of about 21.5°, 19°, 15.5°, and 12.5° (in order of prominence), they appeared to represent a mixture of celluloses II and IV. The RT-treated films showed only two peaks, close together, at around a 2θ angle of around 20–22°. These observations, together with the enhanced peaks in the infrared, indicate the boiling water causes changes in the cellulose crystalline morphology relative to room temperature hydrolysis.

Finally, it should be noted that the trace amounts of unhydrolyzed trifluoroacetate partial esters, observed in the infrared spectra of the RT-hydrolyzed blends, vanish at compositions containing 60% or more cellulose. This is corroborative evidence that the continuous phase changes from PET to cellulose at around the 50/50 composition. Evidently, the diffusion in the films of the water, needed for the hydrolysis, is enhanced by the hydrophilic nature of the cellulose continuous phase.

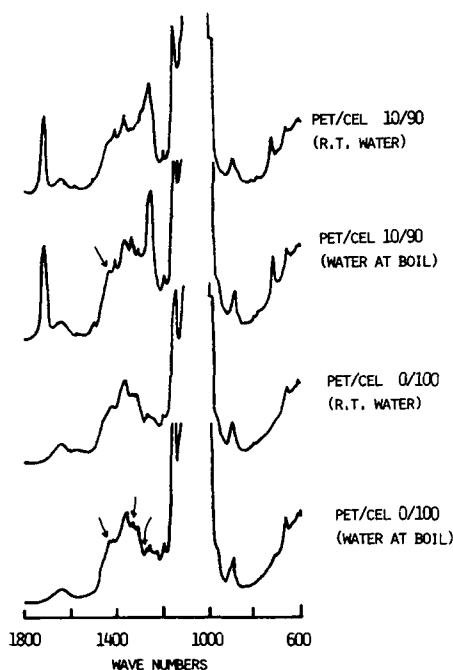


Fig. 5. IR spectra for RT and boiling water cellulose rich films.

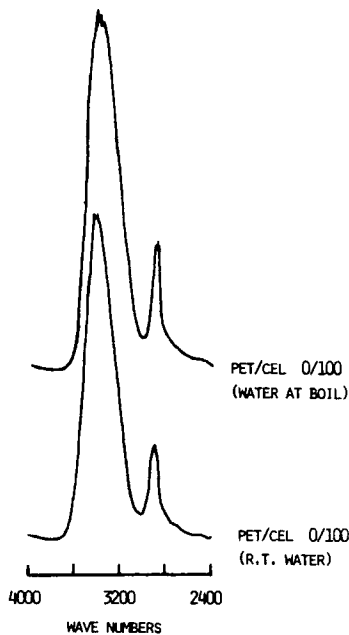


Fig. 6. RT spectra for cellulose-rich films—hydroxyl region.

CONCLUSIONS

1. Films of blends of cellulose and amorphous PET can be prepared by room temperature hydrolysis of films of blends of cellulose trifluoroacetate and PET. Crystallization can be induced by hydrolysis/annealing in boiling water.

2. Crystallization of the room temperature prepared blend is induced during DSC scanning. The peak of the exotherm is shifted to lower temperatures as the cellulose content is increased. Nucleation by the cellulose or the water associated with the cellulose is proposed as an explanation.

3. The crystallization exotherm is diminished with increasing cellulose and vanishes at about 50% cellulose. This can be accounted for by evaporation of the water associated with the cellulose and an inversion of the continuous phase from the PET to the cellulose.

4. Evidence is presented to indicate that the cellulose formed in the room temperature hydrolysis is in a different crystalline state than the boiled cellulose.

5. Additional evidence is presented to indicate that melting and recrystallization of the PET takes place during the DSC scans.

6. Trace trifluoroacetate ester is present in the room temperature hydrolyzed PET-rich samples but absent in the cellulose-rich films. This is interpreted as additional evidence of the phase inversion.

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