Macromolecules **1993,** *26,* 2963–2967

Cellulose Acetate Propionate and Poly(tetramethylene glutarate) Blends

Charles M. Buchanan,* Steve C. Gedon, Alan W. White, and Matthew D. Wood

Research Laboratories, Eastman Chemical Company, P.O. Box 1972, Kingsport, Tennessee 37662

Received June 19, 1992; Revised Manuscript Received March 5, 1993

ABSTRACT: Blends of a polyester, poly(tetramethylene glutarate) (PTG), and a cellulose ester, cellulose acetate propionate (CAP), in the range of 50–90 wt % CAP were prepared by thermal compounding. Carbon-13 NMR and gel permeation chromatography showed that no transesterification and little loss in molecular weight occurred during thermal mixing. Differential scanning calorimetry of PTG and of CAP cooled rapidly from the melt revealed that PTG is a low melting (39 °C), low T_g (−55 °C), semicrystalline polymer while the CAP is an amorphous, high T_g (136 °C) polymer. These CAP/PTG blends are optically clear and, when quenched from the melt, amorphous. Some blend compositions did exhibit small crystallization exotherms and melting endotherms in DSC experiments. The temperature of these melting endotherms decreased linearly from ca. 168 to 148 °C with decreasing CAP content over the range 85–60% CAP, while the ΔH_f reached a maximum at 75% CAP in the blend; the glass transition temperature of these same blends agreed well with predicted values. These results indicate that CAP can crystallize from the solid-state solution under appropriate experimental conditions depending upon the content of amorphous polymer and upon the T_g/T_c gap.

Introduction

Cellulose esters are perhaps one of the oldest and most useful polymers known. In thermoplastic applications, cellulose esters provide materials with a combination of good optical clarity and high flexural, tensile, and impact strengths as well as a high modulus. Although these properties are desirable in many applications, these same properties prohibit their broad use. For example, cellulose esters are not widely used in applications where a low modulus and a high elongation at break is needed such as in film applications.

The most common commercial cellulose esters are cellulose acetates (CA), cellulose acetate propionates (CAP), and cellulose acetate butyrates (CAB). These cellulose esters typically have degrees of substitution (DS) in the range of 2.5–3.0, melting temperatures between 150 and 250 °C, and high melt viscosities. The combination of high melt temperatures and high melt viscosities generally makes the use of plasticizers necessary in order to prevent thermal decomposition during thermal processing. The common plasticizers, generally monomeric in nature, can present many problems including vaporization during melt processing and long-term incompatibility with the cellulose ester.

Recognizing the inherent limitations of cellulose esters when used as thermoplastics, we initiated a program in cellulose ester/polymer blends. Our hope was both to extend the physical properties that can be obtained from derivatives of cellulose and to eliminate the use of monomeric plasticizers. We also believe that some cellulose ester/polymer blends will prove useful as biodegradable polymers. In this context, we point out that the base polysaccharide, cellulose, is a renewable resource commonly derived from wood, cotton, and, more recently, biological fermentations.[1] We have also recently reported that some ester derivatives of cellulose can in fact be degraded by microorganisms.[2]

In a recent report, we described our findings on miscible blends of cellulose acetate butyrate and poly(hydroxybutyrate-*co*-valerate) (PHBV).[3] The CAB/PHBV blends exhibited unusual relaxation in both their calorimetric and viscoelastic spectra as well as useful physical properties. As a continuation of this work, we describe in this account our results from the study of miscible blends of CAP ($DS_{Pr} = 2.65$, $DS_{Ac} = 0.10$) with poly(tetramethylene glutarate) (PTG; Figure 1). In particular, we provide analysis of carbon-13 NMR spectra and molecular weight data as well as present a detailed analysis of the dynamic mechanical thermal (DMTA) and differential scanning calorimetry (DSC) spectra of the CAP/PTG blends.

Experimental Section

Cellulose acetate propionate (CAP482-20) is commercially available and was obtained from Eastman Chemical Co. (Kingsport, TN). Poly(tetramethylene glutarate) was prepared by the condensation polymerization of dimethyl glutarate and 1,4-butanediol using $Ti(O^iPr)_4$ as the catalyst.[4]

Blends were prepared by first mixing the blend components in a plastic bag before compounding at 230 °C in a Rheometrics mechanical spectrometer for 5 min. The resulting blend was ground to 5-mm particle size, and a portion was pressed between two metal plates at 230 °C. Samples for dynamic mechanical thermal analysis were uniform, melt-pressed films prepared using metal plates having a preformed well of 20 mil. The unquenched DMTA samples were allowed to cool at ambient temperature between the metal plates, while the quenched samples resulted from immersion of the metal plates into dry ice/acetone (−78 °C). The quenched samples were stored in dry ice until collection of the DMTA spectrum. The pure blend components were treated in identical fashions. All of the blends were transparent in the melt, after quenching, and after slowly cooling from the melt. Samples stored for over 18 months are transparent and do not exhibit significant loss of physical properties.

GPC data were acquired on a Waters Model 150C gel permeation chromatograph. The mobile phase was $CHCl_3$, and the sample size was 20–25 mg/10 mL. The molecular weights are reported in polystyrene equivalents.

Carbon-13 NMR spectra were collected on a JEOL Model GX 270-MHz spectrometer operating at 67.8 MHz. The spectra were collected at ambient temperature with a sample concentration of 100 mg/mL of $CDCl_3$. The center peak of $CDCl_3$ was used as an internal reference which was taken to be 77.0 ppm. All NMR spectra were processed by using an 8-Mbyte Mac II Macintosh computer, with VersaTerm Pro as an emulation package and MacDraw II as a graphics package, interacting with Hare's FTNMR software running on a VAX 8800 computer.

0024-9297/93/2226-2963$04.00/0

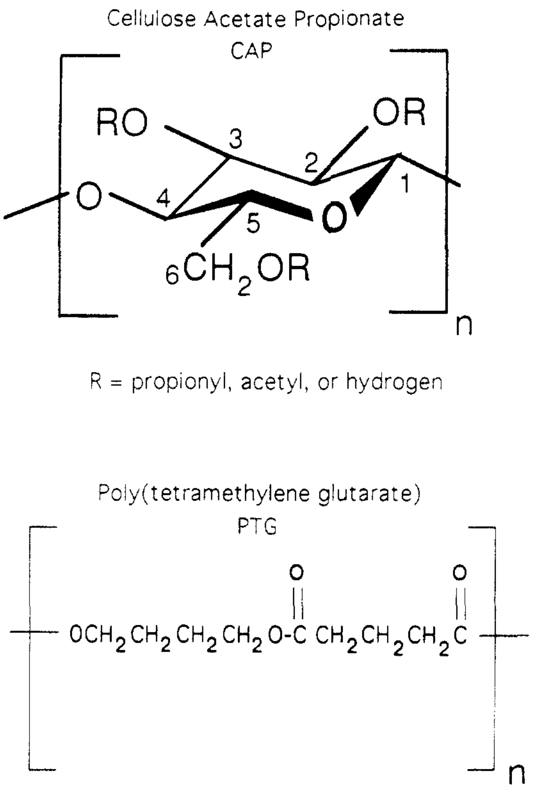

Figure 1. Structures of the cellulose ester and polyester used in this study.

Dynamic mechanical thermal analysis was accomplished using a Polymer Laboratories Mk II spectrometer operating in single cantilever mode at a heating rate of 4 °C/min and a frequency of 1 Hz.

The DSC spectra were collected using a Du Pont 912 differential scanning calorimeter spectrometer. In order to provide the same thermal history, each sample was heated from room temperature to 250 °C at a heating rate of 20 °C/min before cooling at 20 °C/min to −100 °C. Second scan heating curves were then collected by heating from −100 to 250 °C before quenching in liquid nitrogen. The quenched samples were then heated from 40 to 250 °C to give a third heating scan. The reported DSC T_g's were taken from the second scan and are reported as the T_g midpoint. The T_g midpoint was taken to be the midpoint of the tangent between the intercepts formed by extrapolation of the base line preceding and following the transition and the tangent of the transition.

Results and Discussion

From the simplest point of view, miscible polymer blends are considered to be amorphous materials which are microscopically homogeneous and are characterized by a single glass transition temperature when measured by thermal or dynamic mechanical techniques. Partially miscible blends display microscopic heterogeneity and characteristically will display two or more glass transition temperatures intermediate between those of the blend components. Barring similar indices of refraction, partially miscible blends tend to be hazy to opaque in contrast to miscible blends which will generally be clear. Immiscible blends are macroscopically heterogeneous, displaying multiple glass transition temperatures, including those of the homopolymer blend components. The boundary between these various classes of blends is often not well-defined, particularly in cases where compatibilizers are employed to increase interactions between two marginally miscible homopolymers.

Poly(tetramethylene glutarate) is a semicrystalline aliphatic polyester with a low (39 °C) melting temperature. Although the polyester can be handled as a solid at room temperature, the low melting temperature generally prohibits the use of the polymer in conventional thermoplastic applications. However, in contrast to the poly(hydroxybutyrate-*co*-valerate) copolyester used in previous work,[3] this aliphatic polyester does not thermally decompose below 250 °C at an appreciable rate, whereas poly(hydroxybutyrate-*co*-valerate) decomposes in the range of 170–190 °C. Consequently, the range of cellulose esters which can be used for thermal blending with PTG without concern for thermal decomposition of the polyester is greater. For this account, we elected to utilize as the cellulose ester component a commercial cellulose acetate propionate commonly used in thermoplastic applications. This CAP has a T_g of 136 °C which is critical since the T_g of the blends decrease with decreasing CAP content (vide infra). By using a cellulose ester with a high T_g, the range of blend compositions with a T_g above room temperature is increased. This is an important feature when dealing with blends with little or no crystallinity.

Table I. Molecular Weights of CAP, PTG, and CAP/PTG Blends Measured by GPC

entry	blend CAP/PTG	M_n ($\times 10^4$)	M_w ($\times 10^5$)	M_z ($\times 10^5$)	M_w/M_n
1	100/0	5.03	1.63	3.03	3.23
2	90/10	3.00	1.28	2.69	4.28
3	85/15	3.03	1.15	2.48	3.79
4	80/20	2.35	1.25	2.88	4.34
5	75/25	2.41	1.05	2.60	4.33
6	70/30	2.36	1.00	2.47	4.22
7	65/35	1.78	1.10	3.13	6.20
8	60/40	1.78	0.84	2.47	4.77
9	55/45	1.87	0.79	2.34	4.25
10	50/50	1.97	0.80	2.33	4.07
11	0/100	2.33	0.67	1.22	2.89

For a number of experimental reasons, our evaluations of polymer blends are based on thermally compounded blends rather than on solvent-cast blends. Melt mixing best ensures that the state of mixing is closer to equilibrium as opposed to solvent casting which can trap otherwise immiscible pairs into a homogeneous, nonequilibrium state.[5] Furthermore, immiscibility in ternary solvent/polymer/polymer mixtures can be driven by nonsymmetrical binary interactions or by transversing a closed-loop immiscibility region during solvent evaporation.[6] Of course, compounding above the lower critical solution temperature or under the upper critical solution temperature can also lead to false conclusions concerning blend miscibility.[7] We attempt to avoid these complications by visually observing the melt mixture during the compounding stage.

When thermally compounding two polymers, one of which contains hydroxyls and another of which is an ester, there is concern both for molecular weight loss of the blend components and for potential transesterification. The molecular weights of the blends (Table I) as measured by GPC indicate minimal weight loss. Both the downward trend of M_w as the polyester component in the blend increases and the relatively broad polydispersities are due to the differences in molecular weight of the PTG and the CAP. With regard to transesterification, Figure 2 shows the carbonyl carbon resonances for CAP, PTG, a blend prepared by solvent mixing of the two components, and a blend prepared by thermal mixing of the blend components. Within the resolution and sensitivity of the experiment, no evidence was found for transesterification.

Differential Scanning Calorimetry. Figure 3 compares the DSC heating curves of the pure blend components after cooling from the melt at 20 °C/min. The polyester exhibits a T_g at −55 °C and crystallization on

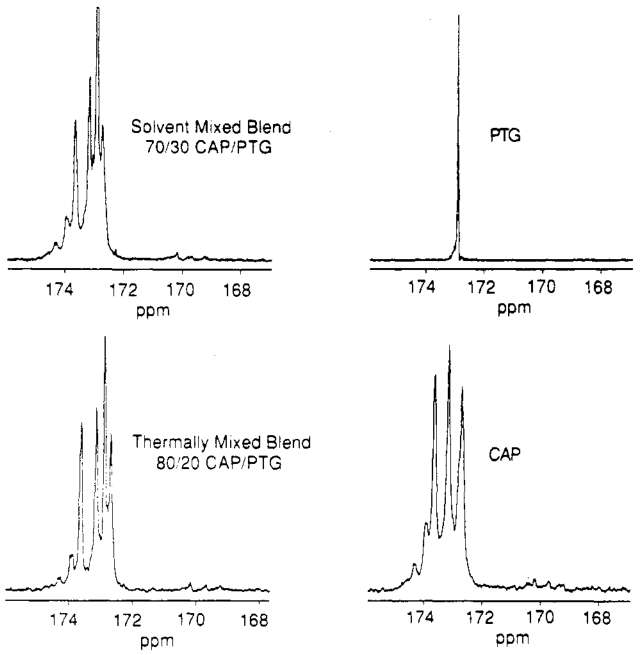

Figure 2. Carbon-13 NMR spectra of the carbonyl carbon resonances of the blend components, of a solvent mixed blend, and of a thermally mixed blend.

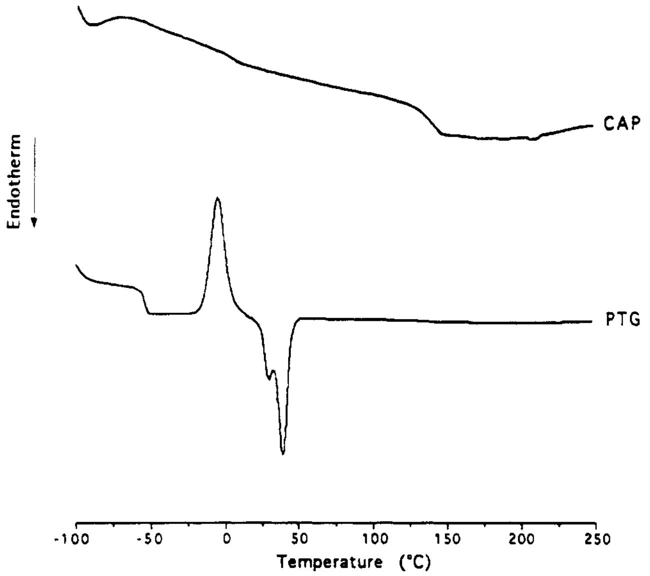

Figure 3. DSC spectra (second scan) of CAP and PTG cooled rapidly from the melt.

heating at −5 °C followed by a melt at 39 °C ($\Delta H_f = 9.28$ cal g^{-1}). Because of the extremely low T_g, the polyester is crystalline when stored at room temperature and, on the first scan, shows a strong melting endotherm but does not exhibit an exotherm due to crystallization. The DSC curve for the CAP on the second scan shows only a glass-to-rubber transition at 136 °C and is thus amorphous after cooling from the melt. The first scan DSC curve of the CAP does show a weak melting endotherm at 202 °C ($\Delta H_f = 2.77$ cal g^{-1}).

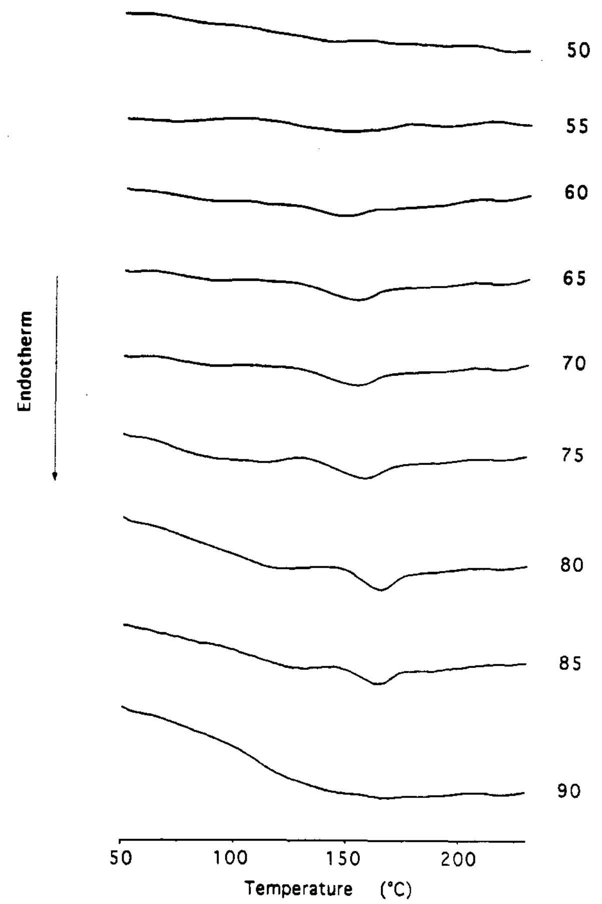

Figure 4. DSC spectra (third scan) of quenched CAP/PTG blends containing 50–90% CAP.

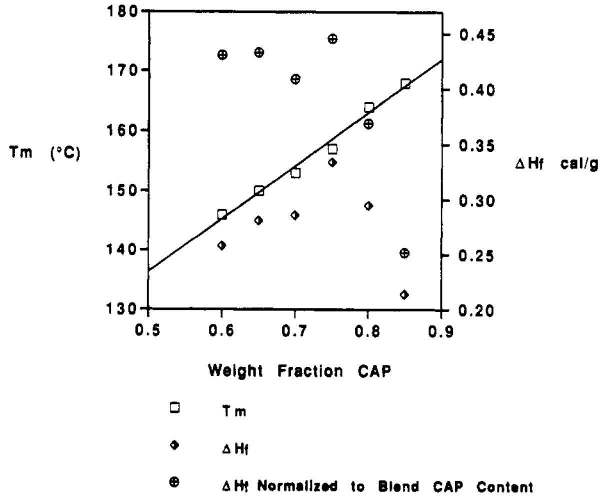

Figure 5. Plot of T_m and ΔH_f (third scan) versus weight fraction of CAP in the CAP/PTG blends.

Figure 4 provides the DSC spectra of the CAP/PTG blends containing 50–90% CAP obtained from quenched (third scan) samples. In these spectra, the T_g for the blends are seen to broaden significantly and become nondescript with decreasing CAP content. The 90% CAP blend remains completely amorphous, whereas in the range of 60–85% CAP the blends show a broad, small, but distinct, exotherm due to crystallization upon heating followed by a melting endotherm. The ΔH_f of the melting endotherm of the quenched samples begin to diminish below 75% CAP, disappearing completely in the 50% CAP blend. Blends containing 40% and 20% CAP (not shown) also showed the complete absence of a crystallization exotherm or a melting endotherm. Figure 5 shows a plot of T_m and ΔH_f (third scan) versus blend composition. The T_m is observed to decrease linearly in the range of 85–60% CAP, dropping ca. 20 °C. The ΔH_f's for the melting endotherms increase with decreasing CAP content, reaching a maximum of 0.33 cal g^{-1} at 75% CAP and then decreasing with decreasing CAP content. When the ΔH_f's are normalized to the CAP content in the blend, ΔH_f is seen to plateau at 75% CAP.

In effect, what we observe is the dilution of a low melting semicrystalline polymer with an amorphous polymer, with the net effect of a very substantial increase in blend melting temperature. This is not a reasonable proposition, as this would require a substantial elevation of the T_m of PTG. In fact, Paul[8] has shown that, in miscible blends involving low melting semicrystalline polyesters with an amorphous, high T_g poly(hydroxy ether) of Bisphenol A (Phenoxy), the observed effect was depression of the blend melting point at lower concentrations of Phenoxy. At high concentrations of Phenoxy (higher blend T_g's), crystallization and melting of the blend was suppressed. Suppression of the T_m occurred because crystallization occurs only when the crystallization temperature is between the blend melting temperature and T_g.[9] Since cocrystallization is extremely rare, we believe that the most likely event is that the CAP is crystallizing from the solid-state solution.[10] Although, CAP is completely amorphous when quenched from the melt, the polyester behaves as a plasticizer providing sufficient mobilization of the CAP to allow selective crystallization of the CAP from the blend. The net result is that we observe a substantial depression of the crystalline melting temperature of the blends over the range of 60–85% CAP, a feature characteristic of semicrystalline–amorphous polymer blends.[11] The 90% CAP blend likely remains amorphous because the blend T_g is approaching the crystallization temperature (T_c).[8,9] At lower concentrations of CAP in the blend (60% <), random placement of the high molecular weight polyester with restricted mobility in the homogeneous melt inhibits crystallization.[11]

Another feature characteristic of semicrystalline–amorphous polymer blends is that, as the content of the diluent (amorphous polymer) in the mixture increases, the total degree of crystallinity substantially decreases.[11] Although we observe a disappearance of crystallinity for blends containing less than 60% CAP, we also observe a maximum in ΔH_f at 75% CAP in the blend; when normalized to the content of CAP in the blend, ΔH_f is seen to plateau at 75% CAP. We believe that these observations reflects the competing effect of a sufficient T_g/T_c gap (<75% CAP) and suppression of crystallization by an amorphous component (60% <CAP).[8]

Dynamic Mechanical Thermal Analysis. The blend components as well as the CAP/PTG blends (unquenched) in the range of 5–50% PTG were subjected to dynamic mechanical thermal analysis (DMTA). The T_g of the blends containing more than 50% PTG lie near or below room temperature and, because they are amorphous, they are tacky and very difficult to handle; no attempt was made to record the DMTA spectra of these blends. Figure 6 shows the storage modulus, E', for nonquenched blends containing 50–90% CAP as well as for the CAP and PTG. The abrupt drop in the storage modulus for CAP is characteristic of amorphous polymers, while the broad, modest change in E' for PTG is characteristic of semicrystalline polymers. Like the parent CAP, the blends exhibit a single relaxation process, with no evidence of a low-temperature transition that could be associated with the polyester.[3,10] The relaxation processes, which are clearly associated with the T_g of the blend, are seen to decrease in a disjointed fashion. The transitions for the blends containing 80–90% CAP, like the parent CAP, are sharp and change monotonically, while the transitions for the blends containing 50–75% CAP are seen to broaden. The mechanical loss tangent, tan δ, for the blends (Figure 7) follows a somewhat similar pattern (for the sake of clarity some spectra were omitted). The loss tangents are observed to shift to lower temperatures and to change both in magnitude and in width. As with E', only a single glass transition temperature is observed; no low-temperature transitions are observed in the region of the polyester.

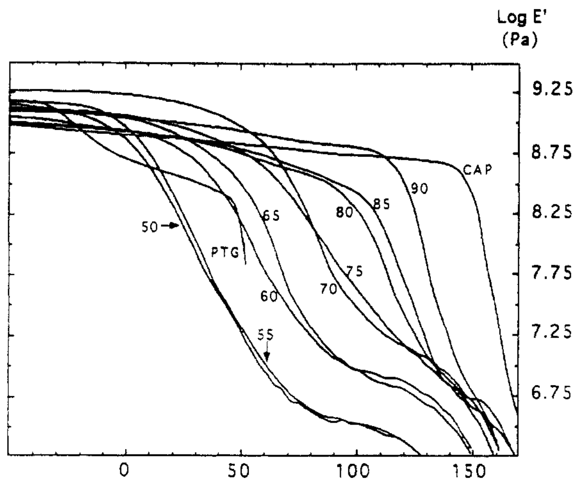

Figure 6. Storage modulus for unquenched CAP, PTG, and blends of CAP/PTG.

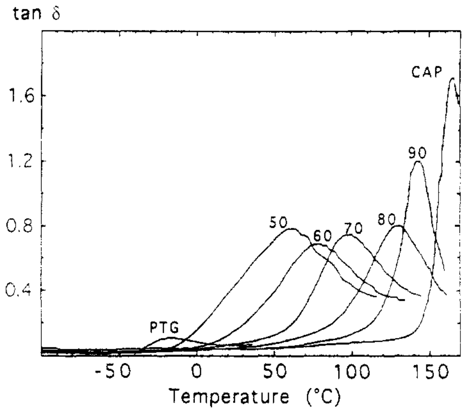

Figure 7. Mechanical loss tangent for unquenched CAP, PTG, and blends of CAP/PTG.

In order to provide a known thermal history, blends containing 55–70% CAP were prepared for DMTA by quenching from the melt at −78 °C (cf. Figures 5 and 8 and Figures 7 and 9). Relative to the unquenched samples, on the basis of intensity and width of the tan δ peaks, the quenched blends are more amorphous; the storage modulus now indicates a stepwise decrease in the glass transition temperature. In addition to a decrease in the width and an increase in the intensity of the tan δ peaks, the tan δ peak maxima are observed to shift to higher temperature for these blends. Also evident from the storage modulus is significant crystallization of the 55% CAP blend. Quenching from the melt provides an amorphous blend, but, relative to the 60–70% CAP blends, the gap between the T_c and T_g of the blend has widened, providing an opportunity for crystallization of the 55% CAP blend under the conditions of the thermal scan (4 °C min^{-1}). Based on DSC, crystallization is to be expected for the 60–70% CAP blends under these conditions as well. However, due to the smaller T_g/T_c gap, what may be occurring is annealing, i.e., slow reorganization, of the crystallites. The net effect would be an increased modulus and lowered damping by the blends, which is what is observed in Figures 8 and 9 for the 70–60% CAP blends relative to the 55% CAP blend.

Figure 10 provides a plot of blend T_g versus blend weight fraction of PTG where the T_g values were taken from the

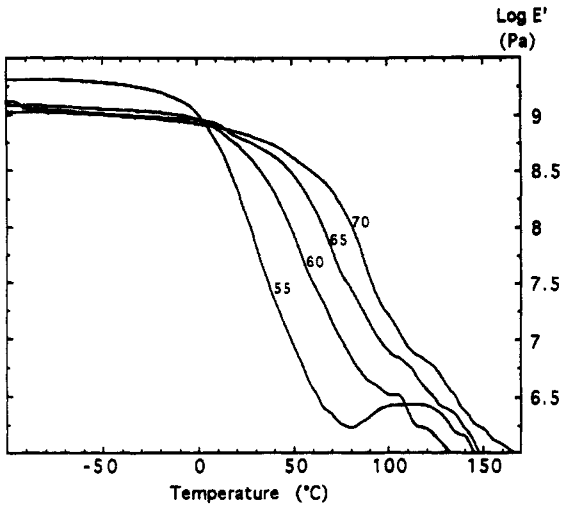

Figure 8. Storage modulus for quenched blends of CAP/PTG.

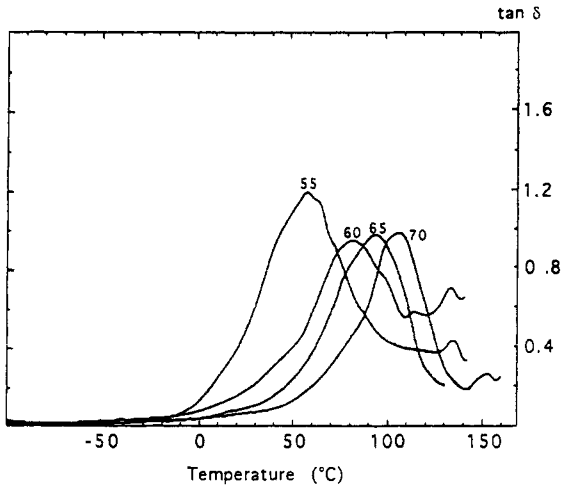

Figure 9. Mechanical loss tangent for quenched blends of CAP/PTG.

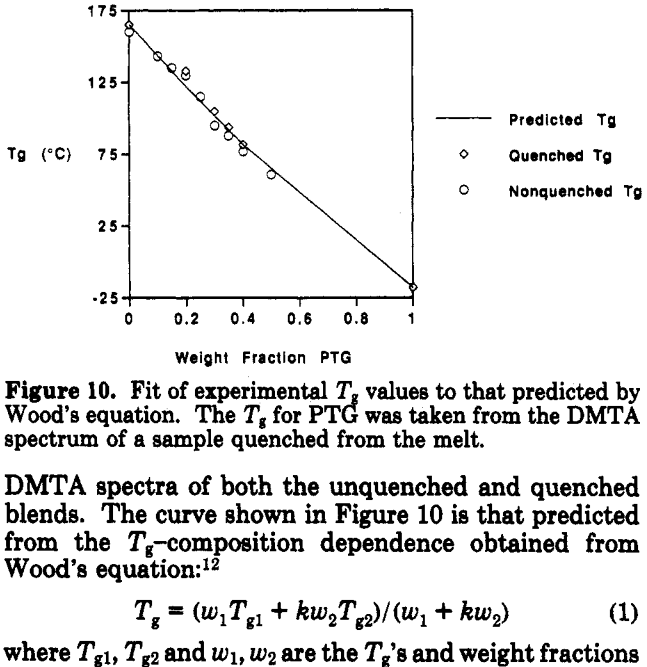

Figure 10. Fit of experimental T_g values to that predicted by Wood's equation. The T_g for PTG was taken from the DMTA spectrum of a sample quenched from the melt.

DMTA spectra of both the unquenched and quenched blends. The curve shown in Figure 10 is that predicted from the T_g–composition dependence obtained from Wood's equation:[12]

$$T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) \qquad (1)$$

where T_{g1}, T_{g2} and w_1, w_2 are the T_g's and weight fractions of components 1 and 2, respectively, T_g is the glass transition temperature of the blend, and k is an adjustable parameter ($k = 0.81$). As Figure 10 illustrates, eq 1 provides a good fit to the experimental data. Some deviation can be expected since the experimental T_g's are taken from broad tan δ peaks. The fit of eq 1 to the experimental data offers good evidence for the miscibility of these blends.

Conclusion

The CAP/PTG blends described in this paper are transparent miscible blends. Data from carbon-13 NMR clearly demonstrate that these blends result from mixing and not from chemical reaction. On the basis of optical clarity, there is no evidence that phase separation occurs in the temperature range of −80 to +230 °C.

These blends, when quenched from the melt, are amorphous. Blends containing 60–85% CAP exhibit small crystallization exotherms and melting endotherms in DSC experiments. The substantial depression of the T_m and the ΔH_f values of the melting endotherms is characteristic of semicrystalline–amorphous blends. The ability of the CAP to crystallize from the solid-state solution is dependent upon the content of the amorphous polymer, the gap between T_g and T_c, and the scanning rate used in the thermal experiment. The blends exhibited single relaxation processes with no evidence of a low-temperature relaxation process which could be associated with the polyester. The glass transition temperatures of the blends gave a satisfactory fit to predicted values for a miscible system. However, because the CAP can crystallize, the experimental method and the degree of crystallinity as well as the thermal history of the blend can influence the value of the glass transition temperature. In closing, the blends described in this report represent a new class of polymer blends. Significant work has been completed in this area and will be detailed in forthcoming papers.

Acknowledgment. Garland Ruth was very instrumental in helping us acquire our DMTA spectra. Barry Pearcy was instrumental in helping us make the polyester.

References and Notes

(1) (a) Johnson, D. C.; Neogi, A. N. U.S. Patent 4,863,565, 1989. (b) Brown, R. M. U.S. Patent 4,942,128, 1990. (c) Brown, R. M.; Liu, F. C. U.S. Patent 4,954,439, 1990.

(2) (a) Buchanan, C. M.; Gardner, R. M.; Komarek, R. J. Aerobic Biodegradation of Cellulose Acetate. *J. Appl. Polym. Sci.* **1993**, *47*, 1709. Presented in part at Cellulose '91, New Orleans, LA, Nov 1991. (b) Buchanan, C. M.; Gardner, R. M.; Komarek, R. J.; Gedon, S. C.; White, A. W. Biodegradation of Cellulose Acetates. *Fundamentals of Biodegradable Polymers and Materials*; Technomic Publishing Co.: Lancaster, Pa, to be published.

(3) Buchanan, C. M.; Gedon, S. C.; White, A. W.; Wood, M. D. *Macromolecules* **1992**, *25*, 7373.

(4) Carothers, W. H. U.S. Patent 2,012,267, 1935.

(5) Barlow, J. W.; Paul, D. R. *Polymer* **1984**, *25*, 487.

(6) Brannock, G. R.; Paul, D. R. *Macromolecules* **1990**, *23*, 5240.

(7) Cruz, C. A.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1979**, *12*, 726.

(8) Harris, J. E.; Goh, S. H.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1982**, *27*, 839.

(9) Rim, P. B.; Runt, J. P. *Macromolecules* **1983**, *16*, 762.

(10) Scandola, M.; Ceccorulli, G.; Pizzoli, M. *Macromolecules* **1992**, *25*, 6441.

(11) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978; Vol. 1.

(12) Wood, L. A. *J. Polym. Sci.* **1958**, *28*, 319.