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Cellulose Ester–Aliphatic Polyester Blends: The Influence of Diol Length on Blend Miscibility

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ABSTRACT: A series of aliphatic polyesters consisting of a C5 dicarboxylic acid (glutaric acid) and C2 to C8 straight-chain diols were blended with cellulose acetate propionate (CAP) at different composition levels. Characterization by dynamic mechanical thermal analysis revealed that, when blended with CAP, the polyesters prepared from C2 to C6 diols formed transparent, stable, amorphous glasses which exhibited a single composition-dependent T_g. Upon reaching a C8 diol, the blend became partially miscible. Within the miscible blends, analysis of their DMTA spectra indicates that the polyester prepared from the C4 diol had the highest level of miscibility with CAP while the polyesters prepared from C5 and $-CH_2CH_2OCH_2CH_2-$ diols gave the lowest degree of miscibility. Sub-T_g mobilization processes, centered in the range −60 to −50 °C, were observed for the blends prepared from polyesters which contained C2, $-CH_2CH_2OCH_2CH_2-$, and C6 diols. The activation energy for the sub-T_g relaxation process (210 kJ mol^{-1}) for the 40% poly(diethylene glutarate)–CAP blend suggests cooperative, localized motion of a CAP–polyester complex. However, no relationship was found between low temperature relaxation processes and blend miscibility.

Polysaccharide derivatives and condensation polyesters represent two of the oldest and, perhaps, most useful classes of polymers available to our society today. Polysaccharide derivatives, such as cellulose esters or ethers, have been known since the middle 1800s and have been commercially available since the early 1900s. Because of this long history, the commercial utility and industrial usefulness of polysaccharides is well established. Although the history of condensation polyesters is not quite so old, since the pioneering work of Caruthers in the 1930s,[1] the embrace of these materials by our society has been remarkable; one only has to study the soft drink industry to understand the influence of polyesters such as poly(ethylene terephthalate). Although these polymers have followed similar paths of growth during this century, rarely have these polymers been chemically or physically combined to provide new and useful materials. This is due, in part, to the inherent incompatibility of polysaccharides to the reaction conditions involved in preparing polyesters. Hence, physical blends of polyesters and polysaccharides perhaps offer the best means of merging these two very important classes of materials. This, of course, assumes that combination of these two classes of polymers will provide miscible polymers blends or, at the least, partially miscible systems with useful physical properties.

In this context, we recently reported that cellulose acetate butyrate (CAB) forms miscible polymer blends with a poly(hydroxybutyrate-*co*-valerate) (PHBV).[2] These CAB/PHBV blends exhibited many useful physical properties as well as very unusual relaxation behavior in their dynamic mechanical thermal spectra (DMTA). In particular, we observed a dual mobilization process, a composition-dependent T_g which corresponded to that of the miscible polymer blend, and a second relaxation process which could be attributed to PHBV.[3] In a different account, we have described our finding concerning miscible polymer blends consisting of cellulose acetate propionate (CAP) and a condensation polyester, poly(tetramethylene glutarate) (PTG).[4] Unlike the CAB/PHBV blends, the CAP/PTG blends exhibited a single composition-dependent T_g corresponding to the miscible blend. In view of ours and others experience with the CAB/PHBV blends[2,3] and the findings of other research groups concerning the presence of sub-T_g relaxation processes in the DMTA spectra of cellulose esters,[5–10] we found the contrast of a single mobilization process in the CAP/PTG blends versus the dual mobilization process of the CAB/PHBV blends intriguing.

In an effort to gain a better understanding of sub-T_g relaxation processes in cellulose ester blends and in order to probe the relationship between polyester structure and blend miscibility in blends involving CAP and aliphatic polyesters, we have prepared a series of polyesters consisting of C5 dicarboxylic acid (glutaric acid) and diol in which the diol is systematically varied from C2 to C8 diol. These CAP/aliphatic polyester blends were characterized principally by dynamic mechanical thermal analysis. The results from this work provide insight into the question of blend component structure–blend miscibility relationships and provide further understanding of mobilization processes in polymer blends.

Experimental Section

Cellulose acetate propionate (CAP482-20), which has a degree of substitution of 2.75 ($DS_{Ac} = 0.10$, $DS_{Pr} = 2.65$), is commercially available and was obtained from Eastman Chemical Co. (Kingsport, TN). Poly(ethylene glutarate) (PEG), poly(trimethylene glutarate) (PTriG), poly(tetramethylene glutarate) (PTG), poly(diethylene glutarate) (PDEG), poly(pentamethylene glutarate) (PPG), poly(hexamethylene glutarate) (PHG), and poly(octamethylene glutarate) (POG) were prepared by the condensation polymerization of dimethyl glutarate and the appropriate diol using $Ti(O^iPr)_4$ as the catalyst.

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. From our experience with many blend systems and mixing techniques, this method of thermal mixing best ensures uniform mixing. The resulting blend was ground to 5-mm particle size, and a portion was pressed between two metal plates at 230 °C. The samples were not dried prior to molding or testing. Samples for dynamic mechanical thermal analysis were uniform melt-pressed films prepared using metal plates having a preformed well of 20 mil. The DMTA samples were quenched from the melt by immersion of the metal plates into dry ice. The quenched samples were stored in dry ice

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until collection of the DMTA spectrum. The blend components were treated in an identical fashion.

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.

Dynamic mechanical thermal analysis (DMTA) was accomplished using a Polymer Laboratories Mk II spectrometer operating in single cantilever mode at a heating rate of 4 °C min^{-1} and a frequency of 1 Hz. For multifrequency experiments, frequencies of 0.3, 3, and 30 Hz were also utilized at a scan rate of 5 °C min^{-1}.

The DSC spectra were collected using a Du Pont 912 differential scanning calorimeter spectrometer. The sample was heated from room temperature to 250 °C at a heating rate of 20 °C min^{-1} before cooling at 20 °C min^{-1} 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.

Results and Discussion

In our prior account concerning blends of poly(tetramethylene glutarate) (PTG) and CAP, we showed that when cooled rapidly from the melt, 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. We demonstrated that these blends, which were prepared by thermal compounding, were transparent, stable amorphous glasses which exhibited a single composition-dependent T_g.[4] 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, indicating that CAP can crystallize from the solid state solution under appropriate experimental conditions depending upon the content of amorphous polymer and upon the gap between the T_g and the crystallization temperature (T_c). Hence, in the blend, crystallization of the polyester is suppressed and, under appropriate conditions, CAP can crystallize. As we shall show, for the compositions studied in this work, PEG, PTriG, PPG, PDEG, and PHG exhibited virtually identical behavior to PTG in blends with CAP; this discussion is deferred until we have examined the DMTA spectra of these blends in detail.

The molecular weights of the CAP, polyesters, and the blends of this study are given in Table I. Because low molecular weight, oligomeric materials can often have some level of apparent miscibility with polymers, our primary concerns were that the polyesters have a high weight average molecular weight (above 30 000), that the polyesters have similar molecular weights, and that the blends be roughly in the same molecular weight range. As Table I illustrates, the weight average molecular weights of the polyesters are in the range 36 000–82 000, roughly half that of the CAP. The weight average molecular weights of the 80/20 blends are all in the range 110 000–126 000 whereas the 60/40 blends have a high molecular weight range, 84 000–125 000. In agreement with prior studies, the values of M_z for the blends indicate that no transesterification has occurred during melt processing.[2,4]

Numerous workers have demonstrated the utility of dynamic mechanical thermal analysis in the study of molecular relaxations of polymers, particularly in the detection of glass-to-rubber transitions (T_g).[11] In a typical DMTA spectrum, traversing the T_g results in a decrease in the storage modulus (E') and a corresponding maxima in the loss modulus (E'') and loss tangent (tan δ). In addition to providing information about the motion of large segments of polymer chains, DMTA also provides information about secondary transitions which occur in the glassy state due to restricted local motions of the macromolecule. With regard to secondary transitions in cellulose esters, workers have reported the presence of a β transition centered from −40 to −35 °C, a β^* transition located above room temperature (typically appearing as a shoulder on the main α transition), and a γ transition usually occurring approximately between −110 and −90 °C.[5,8] Although it has been suggested that the β transition involves rotational motion of the side chain substituents, more recent work has clearly linked this transition to localized motion of the polysaccharide main chain.[5,9,10] The β^* transition is due to water absorbed by the cellulose ester during storage, while the γ transition can be attributed to the motions of water molecules associated with the polymer through polar interactions. In the dynamic mechanical spectra of cellulose mixed esters such as CAP, tan δ typically shows a much smaller effect due to H_2O and the continued presence of the β transition.[8]

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

material[a]	$10^{-4}M_n$	$10^{-5}M_w$	$10^{-5}M_z$	M_w/M_n
PEG	4.32	0.82	1.39	1.92
PTriG	4.24	1.05	1.85	2.46
PTG	2.33	0.67	1.22	2.89
PPG	3.23	0.65	1.02	2.01
PDEG	3.80	0.64	1.01	1.68
PHG	1.59	0.36	0.62	2.29
POG	3.90	0.79	1.26	2.02
CAP	5.03	1.63	3.03	3.23
20% PEG	3.01	1.26	2.71	4.17
20% PTriG	3.33	1.56	4.59	4.67
20% PTG	2.35	1.25	2.88	4.34
20% PPG	4.34	1.38	2.92	3.18
20% PDEG	2.83	1.16	2.60	4.09
20% PHG	2.55	1.10	2.54	4.33
20% POG	3.18	1.19	2.74	3.74
40% PEG	3.30	1.20	2.59	3.62
40% PTriG	4.09	1.34	2.80	3.28
40% PTG	1.78	0.84	2.47	4.77
40% PPG	3.04	1.20	3.05	3.93
40% PDEG	2.82	0.99	2.2	3.51
40% PHG	2.27	0.93	2.59	4.11
40% POG	3.55	1.13	2.29	3.18

[a] PEG = poly(ethylene glutarate); PTriG = poly(trimethylene glutarate); PTG = poly(tetramethylene glutarate); PPG = poly(pentamethylene glutarate); PDEG = poly(diethylene glutarate); PHG = poly(hexamethylene glutarate); POG = poly(octamethylene glutarate); CAP = cellulose acetate propionate.

Figure 1 gives the DMTA spectrum of the CAP used in this work. The large tan δ peak and the associated large drop in the storage modulus at 165 °C can be confidently assigned as the glass transition of the polymer (labeled as the α transition; cf. Table II).[12] The broad shoulder (ca. 50–125 °C), identified by other groups as a β^* transition,[8] is clearly evident. A β transition appears in the tan δ curve (see insert) as a very weak, broad peak centered near −25 °C. Correspondingly, the storage modulus shows a gradual drop from about −75 °C to room temperature and the loss modulus shows a broad maximum. This transition is obviously very weak and reflects only small, local mobilization of the polysaccharide main chain.

Figure 2 provides the storage moduli (E'), tan δ, and loss moduli (E'') for PEG and for PDEG. The intensity of the tan δ peaks for these polyesters reflects the amorphous character of these polyesters; DSC spectra (not shown) of these polyesters do not show melting endotherms. The storage and loss modulus of PEG shows a very broad transition between −80 and −20 °C which we attribute to water absorbed during the quench and during

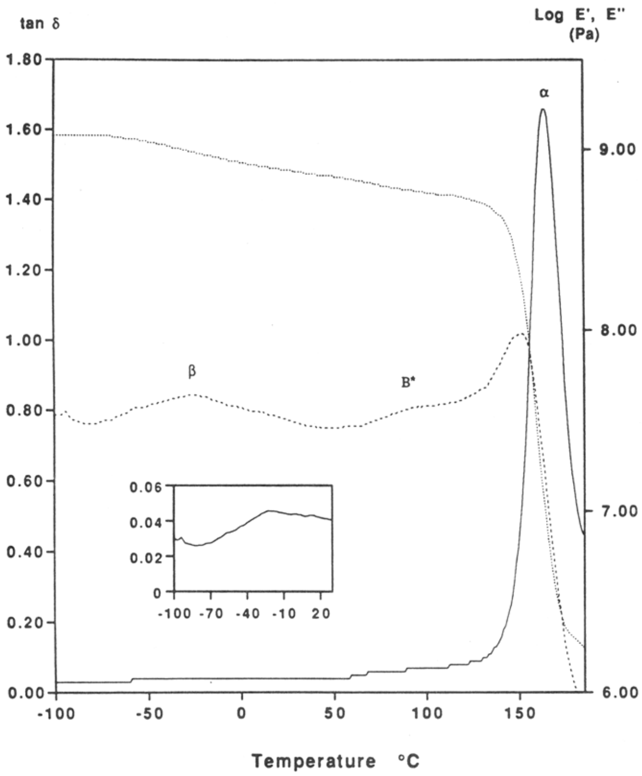

Figure 1. DMTA (1-Hz) spectra of cellulose acetate propionate. The insert is an expanded view of tan δ.

Table II. Glass Transition Temperatures (°C) of the CAP and Polyesters of This Study[a] As Determined from the Peak Maximum of the DMTA tan δ Curve

CAP	PEG	PTriG	PTG	PPG	PDEG	PHG	POG
165	−8	−15	−18	−8	−14	−13	−11

[a] PEG = poly(ethylene glutarate); PTriG = poly(trimethylene glutarate); PTG = poly(tetramethylene glutarate); PPG = poly(pentamethylene glutarate); PDEG = poly(diethylene glutarate); PHG = poly(hexamethylene glutarate); POG = poly(octamethylene glutarate); CAP = cellulose acetate propionate.

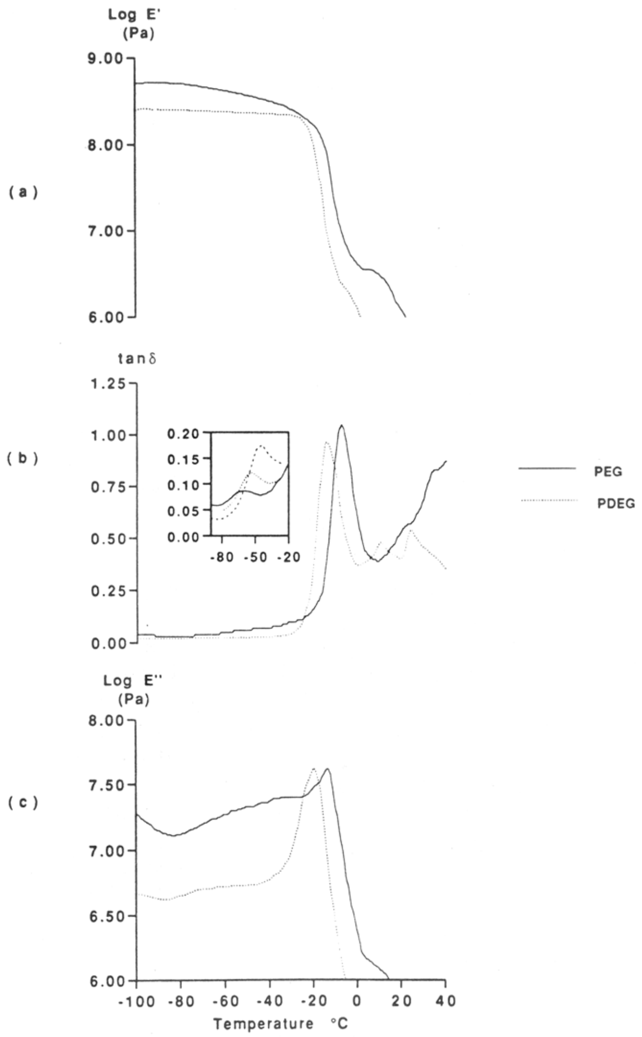

Figure 2. DMTA (1-Hz) spectra of the amorphous aliphatic polyesters: (a) storage modulus, (b) tan δ, and (c) loss modulus. The insert shown shown in the tan δ spectra is of PDEG and is the result of multiple frequency experiments (0.3, 3, and 30 Hz).

storage. Of the polyesters examined, only PDEG showed evidence of a secondary transition (−53 °C at 3 Hz; cf. insert) which was very weak at low frequencies but more intense at higher frequencies. An Arrhenius plot indicated that the activation energy for the sub-T_g relaxation process was 103 kJ mol^{-1} while the activation energy for the α transition was 306 kJ mol^{-1}. The corresponding DMTA curves for PTriG, PTG, PPG, PHG, and POG are shown in Figure 3. The broad, low intensity tan δ peaks and the small drop in the storage moduli are characteristic of semicrystalline aliphatic polyesters. The glass transition temperature of these polyesters as well as the CAP as measured by DMTA are summarized in Table II.[12]

As we have noted, CAP/PTG (C4 diol) blends are transparent and miscible. As Figures 4 and 5 illustrate, the blends containing 20 and 40% PTG show only a single mobilization process at 134 and 81 °C, respectively, with no evidence in either the mechanical loss or moduli of a secondary sub-T_g relaxation. In the following discussion for the other blends involving polyesters prepared from glutaric acid, the DMTA spectra are presented relative to these blends.

Figures 4 and 5 also give the DMTA curves for the other blends containing 20% and 40% polyester. Beginning with the 20% PEG (C2 diol) blend, we see that the tan δ curve has an α transition (T_g) with a peak maximum at 121 °C and that the intensity of the α peak is only slightly less than that of the 20% PTG blend (cf. Tables III and IV). The tan δ curve shows the shoulder commonly associated with the β* transition of cellulose esters, but a β transition is not evident. The storage modulus has a two step drop, and the loss modulus has two corresponding maxima centered at +84 and −17 °C. The maximum in the loss modulus at 84 °C is, of course, related to the T_g of the blend. Given that the peak maximum in the loss modulus of PEG is centered near −14 °C, the broad maximum at −17 °C could be indicative of a phase consisting nearly entirely of PEG or, perhaps, a dual mobilization process similar to that observed with the CAB/PHBV blends. However, this low temperature transition is absent in the 40% blend. Moreover, the neat polyester exhibits a broad sub-T_g transition likely associated with H_2O and the experimental T_g of the blend is very near that of the calculated value. Hence, we believe that the broad low temperature transition in the loss modulus is more likely associated with that of absorbed water. In the 40% PEG blend, the tan δ curve shows a broad T_g centered at 83 °C and a small transition (see insert) near −60 °C; the loss modulus shows the corresponding maxima. The origin of the peak at −60 °C is not immediately evident but a few general observations can be made. First, as we have seen, with the exception of PDEG, neither the polyesters nor the CAP have strong secondary sub-T_g transitions and, in the case of CAP, the

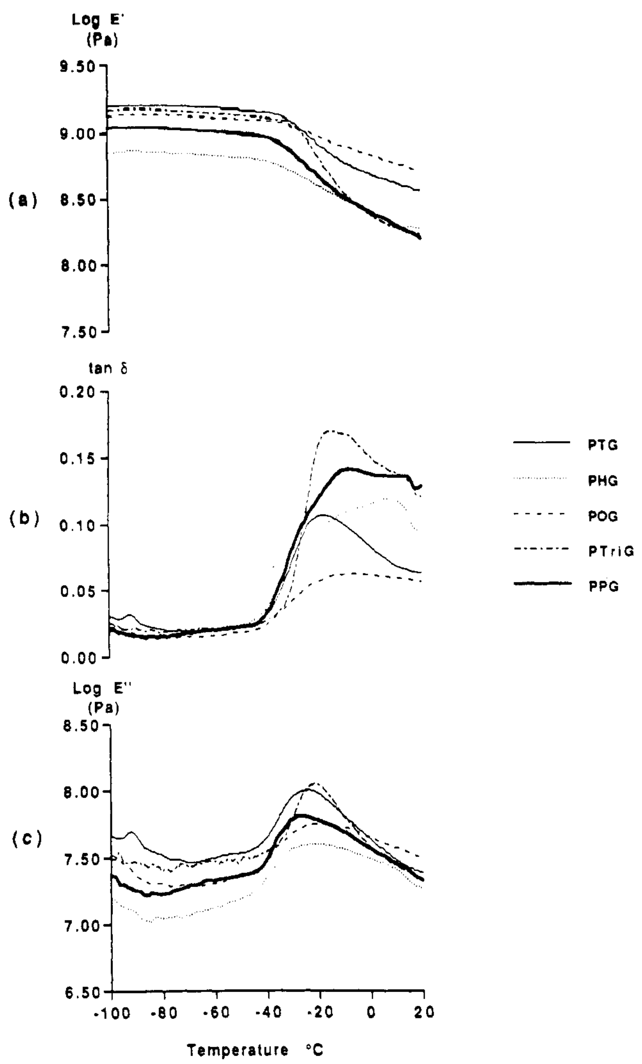

Figure 3. DMTA spectra of the semicrystalline aliphatic polyesters: (a) storage modulus, (b) tan δ, and (c) loss modulus.

sub-T_g transition is ca. 35 deg higher than that observed with the blend. Secondly, the position of this peak appears at too low of a temperature to be associated with the β transition observed with cellulose acetate[5] and at a higher temperature expected for a water–methoyl complex.[8] Likewise, the low temperature peak is not likely associated with rotational motion of the side chain substituents, as the simplest acyl containing polymer (polyvinylacetate) has a relaxation peak for acetate near −100 °C.[13] Finally, we note that Seymour et al. have suggested that plasticization of cellulose esters can often lead to a new peak in the mechanical loss modulus which can be attributed to cellulose ester–plasticizer interaction[8] and that the location of the peak can vary depending upon the characteristics of the plasticizer. In this context, we suggest that the −60 °C peak may in fact arise from CAP–polyester cooperative, localized motion. Unfortunately, the intensity of this peak was too weak for confident measurement of the activation energy of the relaxation process, but the activation energy for a similar peak is presented below.

The DMTA spectra for the 20% and 40% PTriG blends are very similar to the corresponding PTG blends. For example, the peak intensity of the α transition from the tan δ curve is only slightly less than that from the PTG blends (Table IV). The most noticeable difference in the DMTA spectra is in that of the 20% PTriG blend which shows a very distinct drop in the storage modulus and a shoulder on the tan δ curve around 50 °C which is most likely, associated with water.

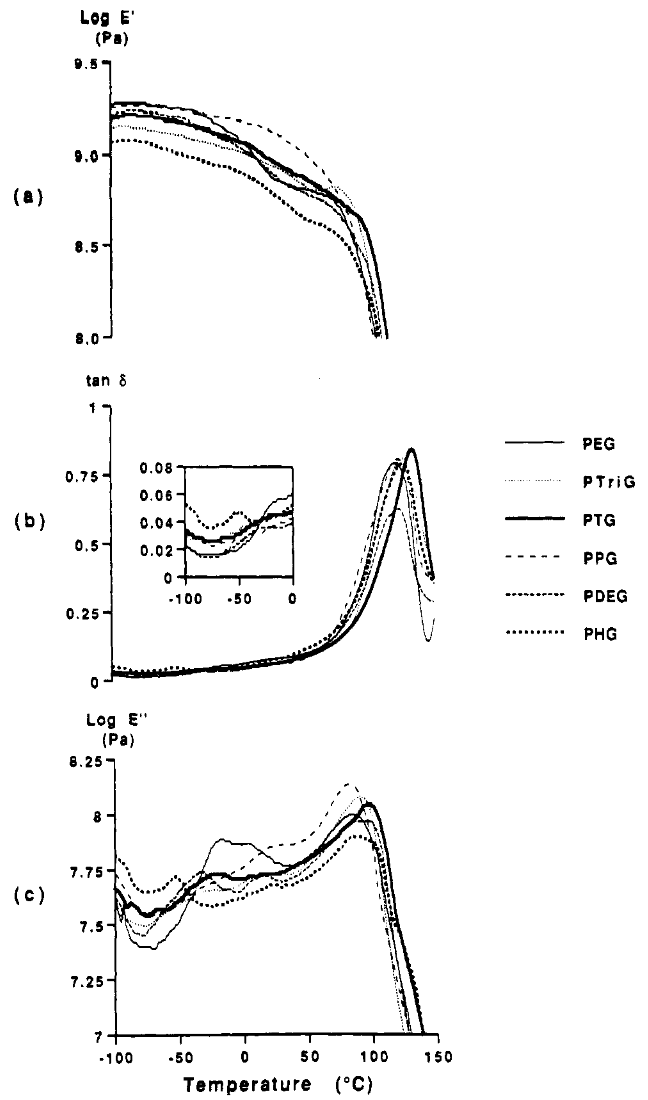

Figure 4. DMTA spectra of CAP blends containing 20% polyester: (a) storage modulus, (b) tan δ, and (c) loss modulus. The insert shown in (b) is an expanded portion of the tan δ curves.

Like PTriG, the diol of PPG contains an odd number of carbon atoms. From Figures 4 and 5, we can see that both the 20% and 40% blends are characterized by a single α transition with no evidence of a sub-T_g transition below 0 °C. Although the temperature range covered by the α transition in the tan δ curve of the 20% PPG blend is greater in the case of the 20% PTriG blend, the peak intensity of the α transition from the tan δ curve of the 20% PPG blend is identical to that of the 20% PTriG blend and only slightly less than that of the 20% PTG blend (Table IV). In the 40% PPG blend, the intensity of the α transition is considerably less than the 40% PTG, being only slightly greater than the 40%, PDEG blend.

The structure of PDEG is similar to that of PPG, the difference being substitution of an oxygen for the center methylene of the diol. From Figure 4 we see that the T_g of the 20% PDEG blend appears at 123 °C; a β transition is not evident from the tan δ curve, while a shoulder on the low temperature side of the α transition is present. Relative to the 20% PTG blend as well as the other 20% blends, the α transition is much less intense. The storage modulus has a three step drop and the loss modulus has three corresponding maxima centered at +96, +15, and −33 °C. The 15 °C transition in the loss modulus is likely related to the β* transition observed in the tan δ curve, but the origin of the −33 °C maximum in the loss modulus is not evident as the corresponding peak in the tan δ curve

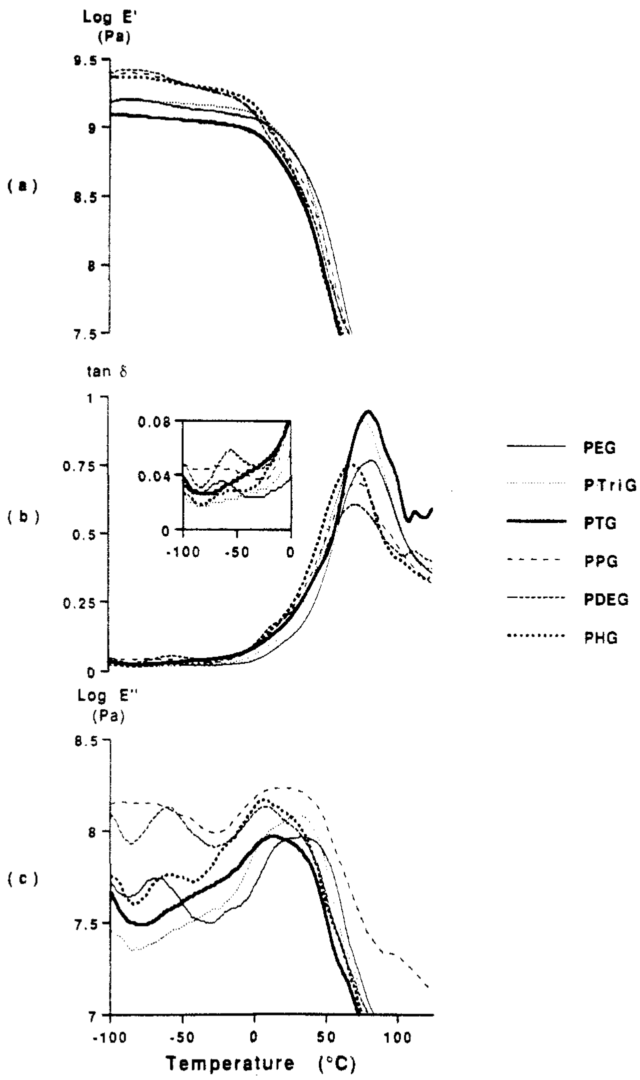

Figure 5. DMTA spectra of CAP blends containing 40% polyester: (a) storage modulus, (b) tan δ, and (c) loss modulus. The insert shown in (b) is an expanded portion of the tan δ curves.

Table III. Glass Transition Temperatures (°C) of the Blends Containing 20% and 40% Polyester along with Estimated T_g Values

blend[a]	T_g (tan δ max)	T_g (cal)[b]
20% PEG	121	120
20% PTriG	124	119
20% PTG	134	122
20% PPG	121	113
20% PDEG	123	113
20% PHG	127	113
20% POG	126, 156	
40% PEG	82	82
40% PTriG	78	78
40% PTG	82	82
40% PPG	72	72
40% PDEG	71	72
40% PHG	71	72
40% POG	90, 155	

[a] PEG = poly(ethylene glutarate); PTriG = poly(trimethylene glutarate); PTG = poly(tetramethylene glutarate); PPG = poly(pentamethylene glutarate); PDEG = poly(diethylene glutarate); PHG = poly(hexamethylene glutarate); POG = poly(octamethylene glutarate); CAP = cellulose acetate propionate. [b] Calculated according to ref 15. The values for *k* were CAP/PEG = 0.74, CAP/PTriG = 0.72, CAP/PTG = 0.81, CAP/PPG = 0.58, CAP/PDEG = 0.62, and CAP/PHG = 0.62.

is broad and ill-defined. In the 40% PDEG blend, the tan δ curve shows a broad T_g centered at 71 °C, a very noticeable shoulder slightly above 0 °C, and a very distinct sub-T_g transition (see insert) near −55 °C; the moduli show the corresponding transitions. The −55 °C transition for the 40% PDEG blend is by far the most intense of any of the sub-T_g transitions observed for the blends. As we have argued above on the basis of peak location, this relaxation peak is likely due to cooperative motion of the CAP and polyester. The activation energy of this transition is 210 kJ mol^{-1}, much higher than that expected for acetate side chain motion (ca. 45 kJ mol^{-1}),[13] nearly twice that measured for cellulose acetate (ca. 100 kJ mol^{-1}), but quite comparable to that of a cellulose acetate plasticized with 50% diethyl phthalate.[6] As we noted earlier, the neat polyester has a transition in this temperature range (−53 °C at 3 Hz) with an activation energy of 103 kJ mol^{-1}, nearly half of that observed in this blend, suggesting participation of both the CAP and polyester in the process.

Table IV. Variation in tan δ Parameters of the Blends as a Function of the Polyester Diol

blend[a]	tan δ[b]	Δtan[c]	Δtan/tan δ[d]
20% PEG	0.80	41	51
20% PTriG	0.81	48	59
20% PTG	0.84	41	49
20% PPG	0.81	60	74
20% PDEG	0.63	50	79
20% PHG	0.79	49	62
40% PEG	0.77	60	78
40% PTriG	0.92	61	66
40% PTG	0.96	51	53
40% PPG	0.69	79	115
40% PDEG	0.61	73	120
40% PHG	0.76	69	91

[a] PEG = poly(ethylene glutarate); PTriG = poly(trimethylene glutarate); PTG = poly(tetramethylene glutarate); PPG = poly(pentamethylene glutarate); PDEG = poly(diethylene glutarate); PHG = poly(hexamethylene glutarate); POG = poly(octamethylene glutarate); CAP = cellulose acetate propionate. [b] Peak intensity at the peak maximum of the tan δ curve. [c] Peak width at peak half-height.[11] For tan δ peaks in which the high temperature side of the curve failed to fall to half-height, the curve was fitted to give a symmetrical curve from which Δtan was calculated.

The peak intensity of the α transition from the tan δ curve of the 20% PHG blend is comparable to that of the 20% PTG blend. The tan δ curve also shows a weak, low intensity peak (also observed in the loss modulus) near −52 °C which, as we have shown above, may be associated with local motions of a CAP–polyester complex. At a level of 40% PHG in the blend, the T_g is observed to shift to 71 °C and the intensity of the transition is observed to be comparable to that of the 40% PEG blend but less than that of the 40% PTG or 40% PTriG blends. The shift to a lower temperature and broadening of the α transition conceals the potential presence of a sub-T_g relaxation process. We do note however, the presence of a weak but distinct maximum in the loss modulus whose position virtually overlaps that of a similar peak in the 40% PDEG blend.

Because the blends involving POG are so uniquely distinct from the other blends presented in this study, we have separated their DMTA spectra from those of the other blends (cf. Figures 4–6). Poly(octamethylene glutarate) is a highly crystalline polyester which, in its DSC spectrum, exhibits an exotherm due to crystallization at 21 °C (ΔH = 17.2 cal g^{-1}) when cooled from the melt at 20 °C min^{-1} and a melting endotherm at 58 °C upon subsequent heating. In Figure 6, we can see that both the 20% and 40% POG blends have a weak transition below 0 °C near that expected for the neat polyester and a small transition centered near 50 °C which we attribute to mobilization due to melting of the POG in the physical blend. This observation is consistent with DSC of the

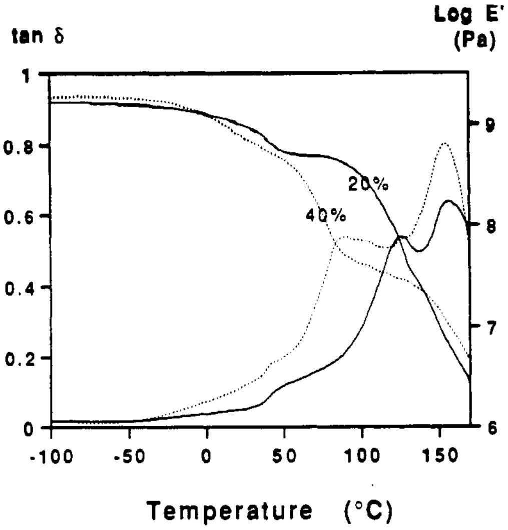

Figure 6. Storage modulus and tan δ for 20% and 40% POG/CAP blends.

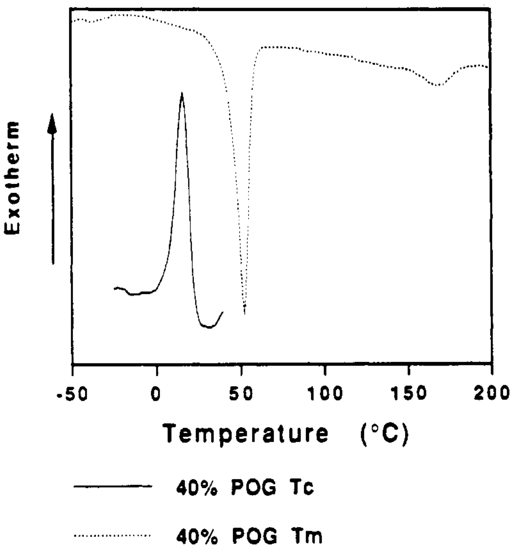

Figure 7. DSC spectra of a CAP blend containing 40% POG.

POG blends. For example, Figure 7 shows the slow cooling curve and second heating curve of the 40% POG blend. On slow cooling (20 °C min^{-1}), the blend exhibits a crystallization peak at 16 °C and, upon heating, a strong melt at 53 °C followed by a weaker melt at 170 °C. Returning to the CAP/POG DMTA spectra, in addition to the transitions at 50 °C, we see that the 20% POG blend shows strong transitions at 126 and 156 °C. The 40% POG blend also shows two very strong transitions, one at 90 °C and another at 155 °C. For the 20% and 40% POG blends, the T_g's estimated by the Fox equation[14] for fully miscible blends are 113 and 72 °C; the reader will also recall that CAP and POG have T_g's at +165 and −8 °C. It seems then that three domains can be identified in this blend system, two separate domains which consist almost entirely of the polyester and the CAP and a third domain which can be related to that for a mixture whose composition is near that expected for a miscible system. Apparently, this blend is not microscopically homogeneous and, upon reaching a C8 diol, crystallization of the polyester is no longer suppressed by the polysaccharide.

The DMTA curves shown in Figures 4 and 5 indicate that quenching of the CAP/PEG, PTriG, PTG, PPG, PDEG, and PHG blends from the melt provides an amorphous glass. DSC curves (not shown) also support that quenching from the melt gives an amorphous glass

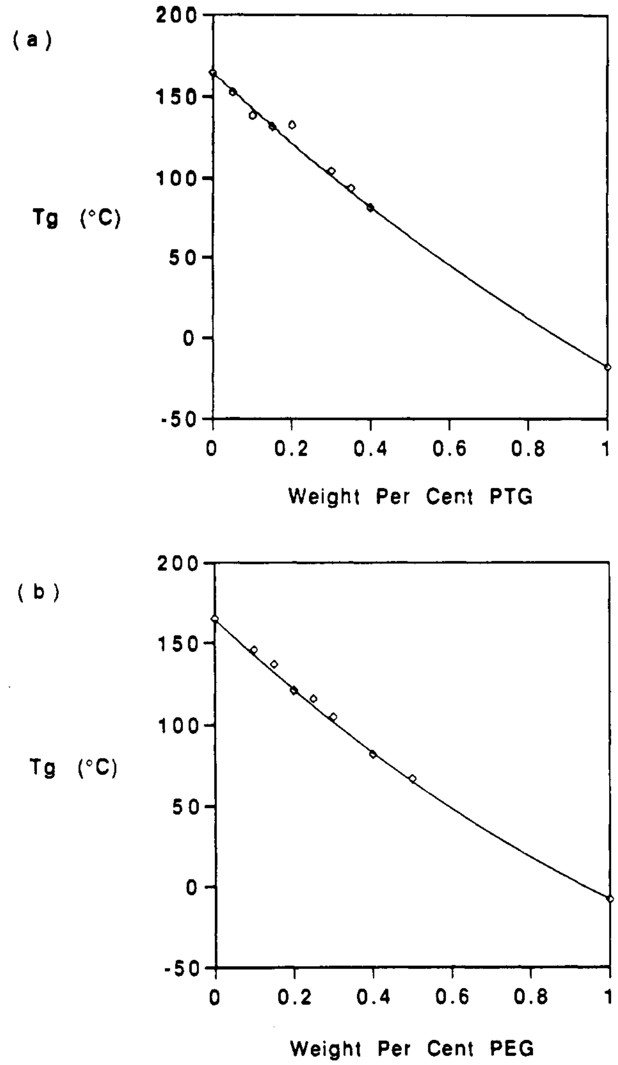

Figure 8. Plots of T_g versus weight fraction of (a) CAP/PTG and (b) CAP/PEG blends. The curves are those predicted by Wood's equation.[15]

which agrees well with what we found with the CAP/PTG blend series.[4] Furthermore, examination of the experimental T_g values shown in Table III reveals good agreement of the experimental T_g with predicted T_g values. For illustrative purposes, Figure 8a,b provides a plot of blend T_g versus weight fraction of PTG and PEG where T_g values are provided over a wide composition range. The curves shown in these figures are those predicted from the T_g–composition dependence obtained from Woods equation:[15]

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

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 and 0.74 for PTG and PEG, respectively). As can be seen from Figure 8a,b, eq 1 provides a good fit to the experimental data, which along with the data contained in Table III, offer very good support for the miscibility of these blends.

At the levels of composition studied, thermal measurements indicate that when quenched from the melt, CAP blends with C2–C6 straight-chain diols and C5 dicarboxylate based aliphatic polyesters provide homogeneous, transparent amorphous glasses. The C8 diol serves as a point of departure from a miscible blend system to a partially miscible system. However, the criterion of a single composition-dependent T_g as a measure of microscopic

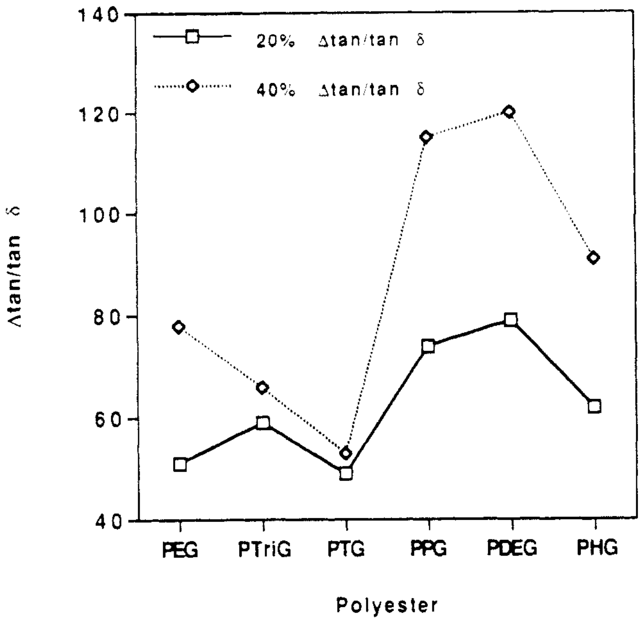

Figure 9. Variations in the relative miscibility of blends of CAP and polyester where the polyester consists of C5 dicarboxylate and the diol is varied from C2 to C6.

homogeneity does not allow one to judge the relative miscibility of the miscible blends. The work of Murayama[11] suggests that the peak intensity and peak width of the damping curve in a DMTA experiment could serve as a measure of blend miscibility. The explicit assumption is that the distribution of the structural relaxation is a reflection of the miscibility of the blend. That is, as the molecular interaction between two polymers in an amorphous blend increases, the α transition would increase in intensity and the width of the transition would become more narrow. Figure 9 shows a plot of $\Delta\tan/\tan\delta$ versus polyester type where $\Delta\tan$ is the peak width at half-height of the α transition in the $\tan\delta$ curve and $\tan\delta$ is the maximum peak intensity of the damping curve. In cases of a nonsymmetrical peak, the curve was fitted to give a symmetrical peak from which $\Delta\tan$ was determined. As can be seen (smaller values indicate "better miscibility"), by this measure for both the 20% and 40% blends, PTG gives the highest level of miscibility with CAP. The polyesters with the shorter diol spacers, PEG and PTriG, have similar levels of miscibility at both levels that are slightly less than that of PTG. However, when the length of the diol is increased from 4 atoms to 5 (i.e. from butanediol to pentanediol or diethylene glycol), the relative miscibility of the blend significantly decreases, particularly at the higher level of polyester. At both 20% and 40% polyester, moving from a C5 diol to a C6 diol results in a return to a "higher degree" of miscibility. This may, in part, be due to the lower molecular weight of the poly(hexamethylene glutarate) used to prepare the CAP/PHG blends (Table I). Further studies on the influence of molecular weight of the polyesters on these blends will be required to clarify this observation.

Conclusions

With the exception of C8 diol polyester (POG), all of the blends of this study provided stable, transparent amorphous glasses when quenched from the melt. These blends exhibited a single composition-dependent T_g. Relative miscibility values determined from the DMTA spectra of the miscible blends indicate that PTG has the highest degree of miscibility with CAP while PPG and PDEG have the lowest degree of miscibility.

With regard to sub-T_g relaxation processes not related to water, the DMTA spectra of CAP blended with 40% PEG, 40% PDEG, and 40% or 20% PHG provided evidence of localized, cooperative motions of a polyester–polysaccharide complex centered around −60 to −50 °C. Evidence for a dual mobilization process such as that observed for the CAB/PHBV blends was not found. Comparison of the relative miscibility values for the blends involving 40% PEG, 40% PDEG, and 40% or 20% PHG offered no suggestion of a relationship between relative blend miscibility and low temperature relaxation processes.

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