Novel Blends of Hyperbranched Polyesters and Linear Polymers

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ABSTRACT: A survey of the phase behavior of blends of hydroxyphenyl- and acetoxyphenyl-terminated hyperbranched polyesters with linear polymers such as polycarbonate, polyesters, and polyamides was carried out. For comparison, blends of poly(acetoxystyrene) (PAS) and poly(vinylphenol) (PVPh) and pairwise combinations of these and the two hyperbranched polyesters were studied. The hydroxy-terminated hyperbranched polyester blend miscibility was identical to that of poly(vinylphenol); this suggests that strong interactions due to hydrogen bonding, more so than chain architecture, dominate the blend miscibility. The acetoxy-terminated hyperbranched polyester showed less miscibility than those hydroxy-terminated polymers due to the absence of strong interactions but still more miscibility than the linear PAS. None of the blends of linear PVPh or PAS with hyperbranched polymer was miscible. However, homogeneous blends of PAS with PVPh and of the two hyperbranched polyesters were observed. In addition, a blend of linear Bisphenol A polycarbonate (PC) with an all-aromatic hyperbranched polyester resulted in increased tensile and compressive moduli and decreased strain-to-break and toughness compared to those of PC.

Introduction

The science and technology of polymer blends has emerged as a major tool for designing and improving polymeric materials. Virtually all classes of commercial polymers have been blended with other polymers to improve physical and chemical properties such as modulus, toughness, processability, barrier properties, and chemical resistance. In general the phase behavior of blends is mainly dependent on the degree of interaction between the constituent polymers determined by their structural groups. Effects of the polymer architecture on the phase behavior, especially those of hyperbranched or dendritic polymers, have still to be examined.

Recently, Fréchet et al.[1] and Turner et al.[2] have synthesized hyperbranched all-aromatic polyesters having terminal 3,5-dihydroxyphenyl or 3,5-diacetoxyphenyl groups in a one-pot synthesis. Despite their high aromaticity, these polymers are soluble in common organic solvents such as THF and DMF. Their aromatic structure imparts to them a high glass transition temperature, T_g, and would be expected to result in a high modulus as well. Blending hyperbranched polymers with linear polymers might be a route to novel materials having improved moduli and heat-distortion temperatures. Such blends would be single or multiphased, depending upon the degree of interaction between the constituent polymers.

Only very few examples of blends with hyperbranched materials are known. Kim and Webster[3] reported the addition of a small amount of hyperbranched poly(phenylene) with the result of somewhat decreased melt viscosity and improved thermal stability in those blends compared to pure polystyrene. However, no details on phase behavior were given. Recently, it has been reported that the addition of small perfect dendritic polyesters[4] and modified hyperbranched polyesters[5] to poly(ethylene terephthalate)[4] or poly(carbonate)[5] can yield miscible blends.

Thus it is of interest to study the phase behavior and other physical properties of all-aromatic hyperbranched polyesters blended with linear polymers. Terminal hydroxyphenyl groups might be expected to interact with other polymers in a manner similar to poly(vinylphenol), PVPh, whose phase behavior and properties have been reported recently.[6,7] It was shown that polyesters containing aliphatic diols and polymers containing strong hydrogen bond acceptors, such as certain polyamides, showed evidence of interactions and miscibility with PVPh.[6,7] Terminal acetoxyphenyl groups are expected to lead to fewer interactions in blends and therefore to less miscibility.

PAS and PVPh were chosen as reasonably close but not exact linear analogs to compare the blend behavior of the hyperbranched structures with those of linear polymers having similar structural groups. To allow a separate look at the effect of polymer–polymer interactions and polymer architecture effects, the two hyperbranched polyesters were blended with a series of linear polymers, mostly polyesters and polyamides, and the data were compared with those obtained in blends of PAS and PVPh with the same linear polymers. Furthermore, the six pairwise combinations of PAS, PVPh, and hydroxyphenyl- and acetoxyphenyl-terminated polyesters were examined.

Even more of interest, from the practical point of view, is the effect of the hyperbranched polymers on the mechanical properties of polymer blends. Some preliminary results could be obtained for tensile and compressive moduli of polycarbonate/hyperbranched polyester blends and will be reported in the following together with the phase behavior of the blends.

Experimental Section

Materials. The structures of the hyperbranched polymers (**P1**–**P3**) studied are shown in Figure 1. The preparation of the hyperbranched hydroxy-terminated polyesters has been described previously.[1,2] For comparison purposes, some blends

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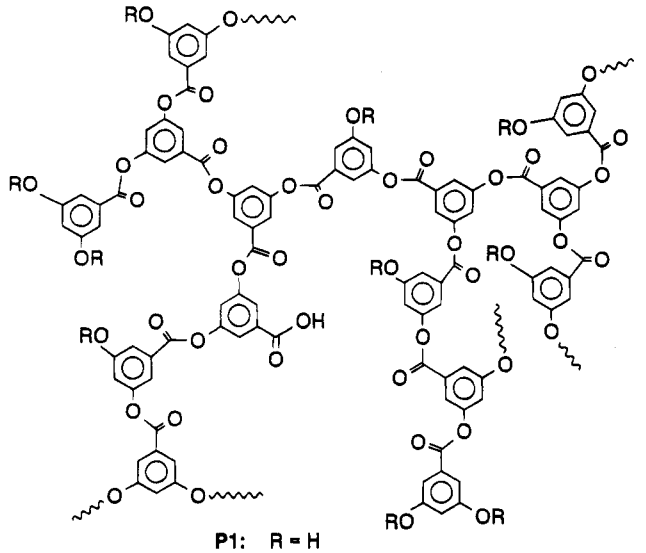


Figure 1. Structures of hyperbranched polymers studied.

Table 1. Hyperbranched Polyester Characterization by SEC[a] and DSC

polymer	terminal groups	M_w	$[\eta]$, dL/g	T_g, °C	ΔC_p, J/(g °C)
P1a	100% hydroxyl	14 000	0.09	206	0.355
P1b	100% hydroxyl	48 800	0.18	195	0.356
P2a	100% acetate	30 000	0.10	145	0.242
P2b	100% acetate	27 000	0.11	142	0.253
P3[b]	90% hydroxyl, 10% acetate	166 000	0.29	196	0.371

[a] SEC = size exclusion chromatography, molecular weights and $[\eta]$ obtained by universal calibration using viscosity detector, eluent = THF.[2] [b] Obtained by hydrolysis of an acetoxy-terminated hyperbranched polyester.

were prepared from hydroxyphenyl-terminated polyesters **P3** that had been obtained by hydrolyzing the acetoxyphenyl-terminated polyesters.[2] Characterization data for the hyperbranched polyesters used in this study are given in Table 1. The variety of linear polymers with which the hyperbranched polyesters were blended are shown in Figure 2, and their properties have been described previously.[6,7] PVPh[8] and PAS[9] have been prepared according to the literature.

Blends Preparation. Solution blends were prepared by dissolving each polymer separately into a common solvent, usually THF, to form a 5 wt % solution. The solutions were then mixed in the final ratio, and the blend was precipitated into an excess of nonsolvent (usually hexane or water). The precipitates were dried in vacuum before analysis.

Melt blends were prepared as follows: Polymers were ground separately in a Retsch grinder or powdered using a mortar and pestle. Samples (4–5 g) were then prepared by hand mixing a 1:3 (hyperbranched to linear polymer) weight ratio. The 1:3 ratio was used because of the high T_g's and low melt strengths of the pure hyperbranched polymers. Following mixing, the blends were dried under vacuum between 95 and 110 °C for at least 24 h prior to extrusion. The polymer blends were extruded through a Microtruder laboratory extruder (Randcastle, Inc.) equipped with a 1/4-in. screw and 2-in. slit die at temperatures ranging from 225 to 280 °C and using a screw speed setting of 75 rpm.

Samples to be melt pressed for mechanical properties were made by hand mixing 22.5 wt % finely powdered hyperbranched polyester with finely powdered polycarbonate (Lexan 145). The blends were dried at 60–80 °C in a vacuum prior to melt pressing. Compression cylinders were made using 1.5 g of polymer in a 1/2-in.-diameter steel mold. Powders were heated to 260 °C and were pressed using 1000–1200 lbs of force, depending on the flow properties of the blend. Sheets were also pressed for tensile testing. Typically, 2.5 g of powder was cold pressed in a 2-in. square steel die using 25 000 lbs of force to fabricate a preform for hot pressing. The green stage preform was hot pressed in a 4.5-in. square steel mold at temperatures around 250 °C using 4500 lbs of force. All samples were pressed between sheets of Upilex S polyimide film to prevent contamination with the steel tooling and to provide a good release surface for the blends.

From previous work[6,7] we know that the miscibilities of precipitated blends versus melt-extruded blends are the same after heating. Therefore we are confident that a melt-extruded blend would have the same degree of phase separation and miscibility as the blends prepared as described above for PC and hyperbranched polyesters. However, the phase morphology in these blends might be different.

Determination of Polymer Phase Behavior and Mechanical Properties. The phase behavior, or miscibility, of the polymer blends was determined by thermal analysis using a Perkin-Elmer DSC7 scanning at a 20 °C/min heating rate. The glass transition temperature, T_g, and the change in heat capacity, ΔC_p, were both determined at the midpoint of the glass transition and reported, typically, for the second DSC trace. The T_g values were determined on quenched, totally amorphous blends. For some samples (compare Tables 2 and 3) there was both a crystallization exotherm and a melting exotherm observed at temperatures above T_g. However, the samples were completely amorphous as quenched through the T_g region and up to temperatures well above the T_g region.

The tensile properties of the blends were determined using the ASTM-III Tensile Test (Small Dogbone) on a Sintech Model 20 Mechanical Testing Apparatus. The engineering stress was calculated using the average cross-sectional area, and the strain was calculated using an effective gauge length of 21.08 mm.

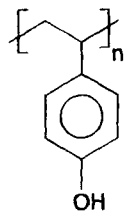
The compression properties were measured according to the ASTM D695m procedure at a constant crosshead speed of 1 mm/min, using the Sintech instrument described above equipped with a 20 000-lb load cell. The samples were cylindrical with an average height of 9.98 mm and a diameter of 12.64 mm. The upper platen has internal bearings to allow some movement, which can compensate for any nonuniformities in the sample height. Young's modulus was calculated using a linear regression of the initial slope of the stress–strain curve, from approximately 0 to 3% strain. The yield stress was calculated at the point at which the slope in the stress–strain curve passed through zero. All compression samples were stopped prior to complete failure.

Results and Discussion

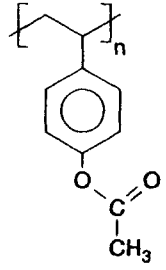
Blend Phase Behavior. The thermal analysis results for blends of 3,5-dihydroxyphenyl- (**P1**) and 3,5-acetoxyphenyl-terminated (**P2**) hyperbranched polyesters with linear polymers are given in Tables 2 and 3. The hydroxy-terminated polymers are miscible with poly(butylene adipate), Trogamid-T, and the copolyester T-C(50)E in blends precipitated from solution and with nylon 6, MXD-6, and T-C(29)E in extruded blends. These results are identical to those seen for blends of the same linear polymers with PVPh.[6,7]

Thermal analysis results for blends of acetoxy-terminated hyperbranched polyesters **P2** with linear polymers show miscibility with poly(butylene adipate) (blend precipitated from solution) and with T-C(29)E (extruded blend). For two of the blends, PC and Trogamid-T, the T_g's of the blend constituents are too close to discriminate by DSC, so no conclusions can be drawn for these from thermal analysis data. Electron micrographs of the compression-molded blend of PC with **P2** show a small amount (much less than 20%) of a distinct separate phase, suggesting that the blend, which is optically clear, is immiscible or only partially miscible.

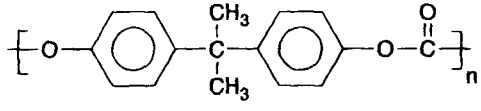
PVPh poly(vinylphenol) T_g = 188 °C



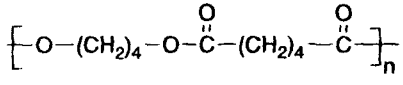
PAS poly(acetoxystyrene) T_g = 127 °C



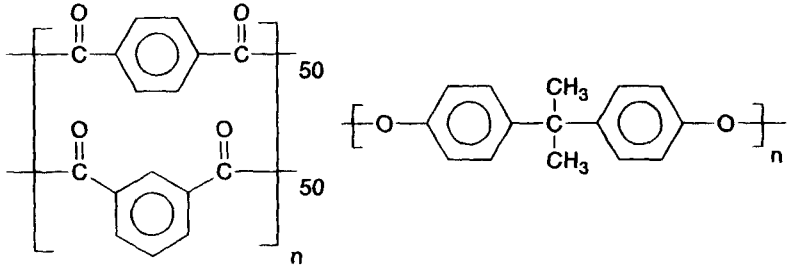
PC bisphenol A polycarbonate Lexan 145 T_g = 152 °C



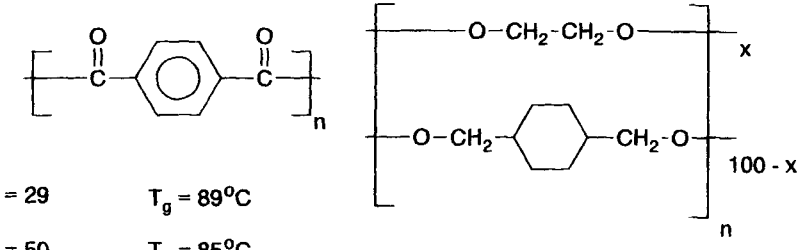
PBA poly(butylene adipate) T_g = -64 °C T_m = 50 °C



T-(50)I-BPA polyarylate Ardel D100 T_g = 193 °C



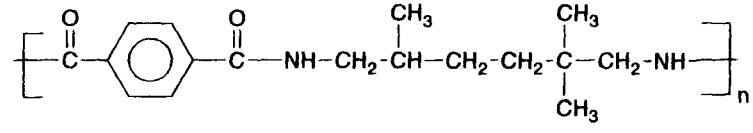
T-C(x)E copolyester



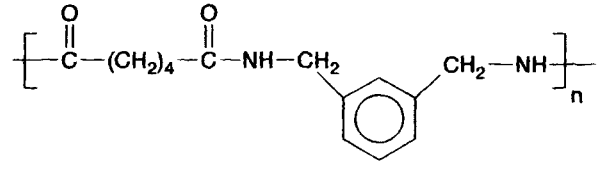
x = 29 T_g = 89°C

x = 50 T_g = 85°C

Trog T polyamide Trogamid T T_g = 154 °C



MXD-6 polyamide T_g = 88 °C T_m = 230 °C



Nylon 6 polyamide T_g = 44 °C T_m = 221 °C

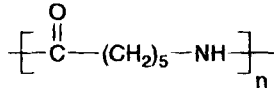


Figure 2. Structures of linear polymers used in blends (T_g values obtained by DSC measurements).

Table 2. Hydroxyl-Terminated Hyperbranched Polyester P1 Blend Miscibility (DSC)

polymer A	polymer B	ratio A/B	prep	T_{g1} onset, °C	T_{g1} midpt, °C	C_{p1}, J/(g °C)	T_{g2} onset, °C	T_{g2} midpt, °C	C_{p2}, J/(g °C)
P1a				198	206	0.355			
P1a	PVPh	1/1	soln	180	185	0.281	205	211	0.123
P1a	PBA	1/1	soln	1	9	0.395			
P1a	Trogamid T	1/1	soln	172	178	0.374			
P1a	PC	1/1	soln	144	148	0.133	211	218	0.123
P1a	T-C(50)E	1/1	soln	126	133	0.329			
P1a	T-(50)I-BPA	1/1	soln	181	187	0.103	203	209	0.115
P1b	T-C(29)E	1/3	melt	109	117	0.272			
P1b	MXD-6	1/3	melt	96	100	0.404			
P1b	nylon 6[a]	1/3	melt	60	64	0.374			

[a] The blend with nylon 6 also exhibits T_m at 192 °C and T_c at 134 °C.

Table 3. Acetoxy-Terminated Hyperbranched Polyester P2 Blend Miscibility (DSC)

polymer A	polymer B	ratio A/B	prep	T_{g1} onset, °C	T_{g1} midpt, °C	C_{p1}, J/(g °C)	T_{g2} onset, °C	T_{g2} midpt, °C	C_{p2}, J/(g °C)
P2a				138	145	0.242			
P2a	PVPh	1/1	soln	142	149	0.080	171	178	0.183
P2a	PBA[a]	1/1	soln	−37	−23	0.350			
P2a	Trogamid T	1/1	soln	136	143	0.343	ind[b]	ind	ind
P2a	PC	1/1	soln	132	138	0.246	ind[b]	ind	ind
P2a	T-(50)I-BPA	1/1	soln	137	145	0.086	168	177	0.071
P2b	T-C(29)E	1/3	melt	91	98	0.240			
P2b	MXD-6	1/3	melt	77	83	0.366	ind[c]	ind	ind
P2b	nylon 6	1/3	melt	ind[d]	ind	ind	107	127	0.132
P2b	nylon 6 (quenched)	1/3	melt	36	43	0.309	ind[e]	ind	ind

[a] The blend with PBA also exhibits T_m at 52 °C and T_c at 33 °C. [b] ind = indeterminate character, constituent T_g's too close to resolve. [c] Second transition obscured by crystallization exotherm: T_m at 216 °C and T_c at 170 °C. [d] Second transition present of indeterminate character. [e] Second transition obscured by crystallization exotherm: T_m at 185 °C and T_c at 104 °C.

Table 4. Blend Miscibility (DSC) of Hyperbranched Polyester P3[a] (1/1 Blends from Solution)

polymer A	polymer B	T_{g1} onset, °C	T_{g1} midpt, °C	C_{p1}, J/(g °C)	T_{g2} onset, °C	T_{g2} midpt, °C	C_{p2}, J/(g °C)
P3		187	196	0.371			
P3	PVPh	181	187	0.290	198	202	0.051
P3	PBA	7.4	27	0.354			
P3	Trogamid T	166	172	0.363			
P3	T-C(50)E	135	143	0.299			
P3	PAS	118	125	0.105	195	201	0.141
P3	**P1b**	181	197	0.349			
P3	**P2a**	162	173	0.293			

[a] Obtained by hydrolysis of an acetoxy-terminated hyperbranched polyester.

Table 5. Blend Miscibility (DSC) of Hyperbranched Polyesters P1 and P2, PVPh, and PAS (1/1 Blends from Solution)

polymer A	polymer B	T_{g1} onset, °C	T_{g1} midpt, °C	C_{p1}, J/(g °C)	T_{g2} onset, °C	T_{g2} midpt, °C	C_{p2}, J/(g °C)
PVPh	PAS	151	158	0.388			
PVPh	**P1a**	180	185	0.281	205	211	0.123
PVPh	**P2a**	142	149	0.080	171	178	0.183
PAS	**P1a**	113	121	0.160	193	202	0.185
PAS	**P2a**	116	124	0.167	144	151	0.091
P1b	**P2a**	156	166	0.317			

PAS is not miscible with any of the linear polymers in Figure 2, but with PVPh (see Table 5).

To verify that hydroxy-terminated hyperbranched polyesters have essentially the same blending behavior irrespective of whether they derive from TMS-protected polymers[1,2] or from the hydrolysis of acetoxy-terminated polymers[2] (approximately 90% of the acetoxy groups are hydrolyzed to terminal OH groups), a series of blends was prepared from the latter (**P3**) with the results reported in Table 4. By comparing these data with those of Table 2, it can be seen that not only are the two hydroxy-terminated hyperbranched polyesters derived from different synthetic pathways miscible with each other but they also exhibit identical blend phase behavior with other polymers.

The results for the six pairwise blends of PVPh, PAS, and the two hyperbranched polyesters show that miscibility is observed only between each hydroxyl-containing polymer and its exact acetylated analog. As shown in Table 5, only the two blends—**P1** with **P2** and PVPh with PAS—are miscible. In other words, hyperbranched polyesters were miscible with each other and the linear pairs were miscible, but none of the four mixtures of hyperbranched and linear analogs was miscible.

Discussion of Blend Thermal and Phase Behavior. The fact that the hydroxy-terminated hyperbranched polyester shows the same general phase behavior as PVPh[6,7] in blends with linear polymers suggests that for most of the blends examined hydrogen bonding is more important than polymer architecture in determining phase behavior. Both the linear and hyperbranched hydroxyl-containing polymers are miscible with hydrogen-bonding acceptors such as polyamides and polyesters derived from aliphatic diols and amines. Neither is miscible with aromatic polyesters and polycarbonates. This conclusion is further sup-

Table 6. Observed versus Calculated T_g's (Midpoint) Using the Fox and Couchman Equations for Blends with Hyperbranched Polyesters P1 and P2

polymer A	polymer B	ratio A/B	C_p of polymer B pure, J/(g °C0	measd T_g, °C	Fox T_g,[a] °C	Couchman T_g,[a] °C
P1b	**P2a**	1/1	0.242	166	168.6	174.1
P1a	PBA	1/1	0.480	9	18.0	24.4
P1a	Trogamid T	1/1	0.400	178	178.5	177.7
P1a	T-C(50)E	1/1	0.240	133	136.8	152.9
P2b	PBA	1/1	0.480	−23	5.0	−8.2
P1b	T-C(29)E	1/3	0.250	117	110.7	120.2
P1b	MXD-6	1/3	0.440	100	109.9	108.5
P1b	nylon 6	1/3	0.410	64	71.8	73.0
P2b	T-C(29)E	1/3	0.250	98	100.9	101.7

[a] Calculated according to eqs 1 and 2.

ported by the fact that neither the acetoxy-terminated hyperbranched polyester nor poly(acetoxystyrene) is miscible with most of the same series of linear polymers, a result which is consistent with the absence of strong interactions in the acetoxy blends.

There are some exceptions to the above generalizations. First, there is the observed miscibility of two blends of **P2**: a melt-extruded blend with T-C(29)E and a solution-precipitated blend with poly(butylene adipate) (PBA). While no strong interactions would be present in either of these blends, two alternative explanations of their miscibility come to mind. The PBA blend may owe its miscibility to a balance of interactions among the functional groups, the so-called copolymer effect.[10-12] The miscibility with PC and similar materials of a variety of aliphatic polyesters containing a certain range of methylene groups has been accounted for using the copolymer balance of interactions effect.[13] This effect may also be pertinent to the miscible melt-extruded polyester blend, although one cannot rule out the possibility that transesterification occurred during melt extrusion, which would also promote miscibility.[14]

The other exception to the above generalization is the observation that the OH-terminated and acetoxy-terminated hyberbranched polyesters are miscible with each other and PVPh and PAS are miscible with each other, but none of the four mixtures of hyperbranched and linear analogs shows one phase. It appears that in those four cross-blends, the intermolecular interaction is not sufficient to overcome the fundamental chemical and architectural differences between the hyperbranched and the linear constituents, even though hydrogen bonding is possible in three of the blends. By themselves, these results suggest that architecture plays a role in polymer blend miscibility. The fact that many other blends of linear with hyberbranched polymers reviewed above are miscible suggests that differences in miscibility are not purely of architectural origin, however, but that chemical structure and interaction are important. Chemical structure effects might be minimized if, for example, the blend properties of PVPh and PAS were compared with those of hydroxy- and acetoxy-terminated poly(phenyleneethylene) or hyperbranched poly(phenylene), which are closer analogs to these linear polymers. The latter might be available from the bromo-terminated hyperbranched poly(phenylene)s published by Kim and Webster.[3] Such a comparison would allow a more unequivocal test of the role of molecular architecture, essentially separate from chemical structure.

Another way to examine the nature of the intermolecular effects in miscible blends is to compare the observed T_g's with those expected from predictions[15,16] (Fox and Couchman equations) based solely on the thermal properties of the separate constituent polymers as shown below. Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{1}$$

Couchman equation:

$$\ln T_g = \frac{w_1 \Delta C_{p_1} \ln T_{g_1} + w_2 \Delta C_{p_2} \ln T_{g_2}}{w_1 \Delta C_{p_1} + w_2 \Delta C_{p_2}} \tag{2}$$

where w_i is the weight fraction and ΔC_{pi} is the change in heat capacity at T_g (K) of the ith component.

In some strongly interacting blends, such as PVPh with poly(4-vinylpyridine), for example, the T_g goes through a maximum with blend composition, presumably owing to strong interactions between the two constituent homopolymers.[17] There have been various theories and empirical equations proposed to account for positive deviations from additivity in polymer blend T_g's.[18,19] We have observed in previous poly(vinylphenol) blend studies, however, that many miscible blends do not show positive deviations from additivity, even though specific interactions via hydrogen bonding are present, as determined by IR spectroscopy.[6] The data in Table 6 show that in no case does the T_g of a hyperbranched polymer blend exceed the Couchman equation (2). Indeed, all but one blend T_g lies at or below the values calculated from the Fox equation (1), which predicts the lower blend T_g's for this system. These results differ somewhat from those for all-linear blends with poly(vinylphenol) in which most of the blend T_g's lie within or above the range predicted from the Fox and Couchman equations.[6,7] The significance of these differences in blend T_g behavior between all-linear and linear−hyperbranched blends is not clear at present. Probably, a more important observation is that none of the blends, either all-linear or linear−hyperbranched, shows positive deviations from additivity exceeding 3 °C. Thus, conclusions regarding the true nature of the intermolecular interactions present in these systems must wait further investigations by other methods, such as infrared spectroscopy or solid-state NMR.

Mechanical Properties of Blends Consisting of Hyperbranched Polyesters and PC. Owing to their high aromaticity and stiffness, the hyperbranched polyesters of this study would be expected to have high moduli. As a result, these polymers might serve as molecular reinforcing agents for blends. To test this hypothesis, as well as to gain information about the hyperbranched polymers themselves, we examined the mechanical properties of two different blends of 22.5 wt % hyperbranched polyester—**P1** and **P2**—with polycarbonate (PC). As discussed above, these blends are both

Table 7. Results of Mechanical Measurements (Tensile) for Polycarbonate/Hyperbranched Polyester Blends

polymer A	polymer B	elongation at break, %	yield stress, MPa	modulus, MPa
PC		82.2	56	1650
PC	**P2**[a]	2.7	46	1890
PC	**P1**[a]	2.9	52	2180
	P2[b]			3050
	P1[b]			6400

[a] 22.5% **P1** or **P2**, 77.5% PC. [b] Moduli calculated for the pure hyperbranched polyesters **P2** and **P1** using eqs 3–7.

Table 8. Results of Mechanical Measurements (Compression) for Polycarbonate/Hyperbranched Polyester Blends

polymer A	polymer B	yield stress, MPa	modulus, MPa
PC		82.7	1460
PC	**P2**[a]	89.9	1570
PC	**P1**[a]	90.4	1680
	P2[b]		2040
	P1[b]		2740

[a] 22.5% **P1** or **P2**, 77.5% PC. [b] Moduli calculated for the pure hyperbranched polyesters **P2** and **P1** using eqs 3–7.

phase separated, although the blend of PC with the acetoxy-terminated hyperbranched polyester **P2** is optically clear. The moduli were analyzed using the Lewis–Nielson equation, given below, which applies to polymer blends and composites:[20]

$$\frac{M_c}{M_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \tag{3}$$

where M_c and M_1 are the moduli of the composite and the matrix, respectively (Young's tensile modulus E, shear modulus G, etc., depending on the geometry), and $A = k_E - 1$, k_E being Einstein's ratio, which is 2.5 for spherical particles. For polymers containing spherical particles, a better expression for A is

$$A = \frac{7 - 5\upsilon_1}{8 - 10\upsilon_1} \tag{4}$$

where υ_1 is the Poisson ratio of the matrix. Other terms in eq 3 are given as follows:

$$B = \frac{M_2/M_1 - 1}{M_2/M_1 + A} \tag{5}$$

$$\psi \approx 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right)\phi_2 \tag{6}$$

or

$$\psi\phi_2 \approx 1 - \exp\left(\frac{-\phi_2}{1 - \phi_2/\phi_m}\right) \tag{7}$$

where M_2 and M_1 are the modulus of the filler and matrix, respectively, ϕ_2 is the volume fraction of filler, and ϕ_m is the maximum possible volume fraction of filler, which is limited by particle packing and geometry. These equations were used initially to estimate how much hyperbranched polymer we would have to add to make a significant difference in the modulus. Conversely, it can be seen from eqs 3 and 5 that, knowing the ratio of the blend and matrix moduli, one can calculate the ratio of modulus of the hyperbranched polymer to that of PC. Since the hyperbranched polymers themselves are quite brittle, this indirect method offered a route to determine some of their properties that might otherwise be difficult or impossible to obtain.

The results of the blend mechanical properties measurements are given in Tables 7 and 8. Blending PC with **P1** and **P2** increases the tensile modulus by 32% and 15% for hydroxy- and acetoxy-terminated hyperbranched polyester blends, respectively. The tensile elongation at break decreased from 82% to just under 3% for both blends. The compression moduli increased by 15% and 7.5% for **P1** and **P2** blends, respectively. Increased moduli and decreased break extensions are typical results for reinforced polymers.[20] The hyperbranched polyesters act effectively as reinforcing agents in the blends.

Given the blend results in Tables 7 and 8, it is a matter of algebra to substitute the various parameters into eq 3 and solve for the ratio of the modulus of hyperbranched polymer to that of PC. For PC, υ_1 is 0.39,[21] so that, from eq 4, $A = 1.232$. Following Nielson, a value of 0.637 for ϕ_m was used, which is that estimated for random close packing.[20] To calculate the volume fractions from the weight fractions, a density of 1.20 was used for PC,[21] and densities of 1.361 and 1.360 were estimated for **P1** and **P2**, respectively, based on group addivity factors from Van Krevelen.[21] Using these densities, the volume fraction of hyperbranched polymer ϕ_2 was estimated to be 0.204 for both blends. As shown in Table 7, the tensile modulus of the hydroxy-terminated hyperbranched polyester is calculated to be 3.9 times that of PC, while the tensile modulus of the acetoxy-terminated hyperbranched polyester is 1.9 times that of PC. The higher moduli are consistent with the greater aromatic character of the hyperbranched polymers. The fact that **P1** has a higher modulus than **P2** is consistent with the fact that the acetoxy group typically shows sub-T_g relaxations that lower the room-temperature modulus.[22] Table 8 also indicates that the compression moduli of the two hyperbranched polymers are increased over that of PC. The proportionate increases are less, about half those observed in tension, which may be related to the fact that rigid polyesters, while strong in tension, are relatively weak in compression.[23]

Summary and Conclusions

A survey of the phase behavior of blends of both hydroxy-terminated and acetoxy-terminated hyperbranched polyesters with a variety of linear polymers was carried out. In addition, the mechanical properties of two hyperbranched/linear blends were examined. The hydroxy-terminated hyperbranched polyesters blend miscibility with linear polymers was identical to that of PVPh, independent of the hyperbranched polyester synthetic method. This indicates strong interactions due to hydrogen bonding, more so than chain architecture, dominate the blend miscibility in these blends. The acetoxy-terminated hyperbranched polyesters show less miscibility than those with hydroxy end groups, which is consistent with the absence of strong interactions in this case. Blends of a linear poly(acetoxystyrene) (PAS) with linear and hyperbranched polymers were prepared as a comparison with their hyperbranched analogs. PAS was least interactive of all, being miscible only with linear PVPh. Furthermore miscibility was found in blends of the two hyperbranched polyesters and in those of PAS with PVPh but none of the blends of linear analog with hyperbranched polymer was single phased.

This indicates that, when chemical structure differences are minimized, chain architecture differences may lead to blend immiscibility.

The mechanical properties of two immiscible blends of linear polycarbonate (PC) with all-aromatic hyperbranched polyesters **P1** and **P2** showed increased tensile and compressive moduli and decreased strain-to-break and toughness compared to unmodified PC. These results allow the conclusion that the aromatic hyperbranched polyesters act as reinforcing agents for polycarbonate. From the blend moduli, the corresponding moduli of the hyperbranched polymers have been estimated. The hydroxy-terminated hyperbranched polymer had about 4 times the tensile modulus and twice the compressive modulus of PC. These properties indicate that blending with all-aromatic hyperbranched polymers should lead to greater hardness and elevated heat-deflection temperatures when compared with unmodified polymers.

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