A miscibility survey of bisphenol A carbonate cyclic oligomers with a spectrum of glassy polymers

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Bisphenol A (BPA) carbonate cyclic oligomers have been found to be miscible with a wide spectrum of glassy polymers from polystyrene to aromatic polysulfones. The surprising breadth of the cohesive energy density (CED) range corresponding to this spectrum is roughly comparable to the breadth of the CED range of small molecule solvents that swell a given glassy polymer heavily, and much smaller than the breadth of the CED range of miscibility seen in a polymer/polymer blend series. Possible sources of this behaviour are indicated.

(Keywords: miscibility; cyclic oligomers; carbonate)

Introduction

Although the synthesis and polymerization of BPA carbonate cyclic oligomer (BPACY) have been the subject of several papers[1-3], the physico-chemical behaviour of these materials as neat substances or in blends with other polymers has received very little attention. The potential for obtaining blends with novel melt rheologies, altered glass transition temperatures (T_gs) and useful mechanical properties, with or without polymerization of the oligomers, has made such blends an interesting subject of research.

This note summarizes a brief survey of the miscibility of BPACY in a spectrum of glassy thermoplastics. This spectrum covers the range of cohesive energy densities (CEDs) from 285×10^6 to 527×10^6 J m^{-3}. Some observations of the effects of resin molecular weight in one system are also reported.

Experimental

Materials. The synthesis of BPACY is described elsewhere[1-3]. Absolute molecular weight averages determined by h.p.l.c. were determined to be: $M_n = 1140$, $M_w = 1530$ and $M_z = 2230$. The polymers used are listed in *Table 1*. More information about them has been reported before[4].

Blend preparation. The casting of a solution of BPACY slowly at low temperatures results in the crystallization of a significant fraction of the oligomers. Therefore, blends of BPACY with other polymers were cast from solution of high boiling point solvents at about 160°C. In most cases, the solvent used was *o*-dichlorobenzene (DCB). A few of the more polar polymers investigated required the use of a mixture of DCB with a more polar solvent such as dimethyl acetamide or dimethyl sulfoxide. Films were dried under vacuum at temperatures between 100 and 140°C for at least 3 days.

A 50/50 blend of BPACY with poly(xylylene ether) (PXE) was also prepared via melt mixing followed by compression moulding. The PXE used was prepared using a manganese-based catalyst system[5,6], since the amine residues present in conventional, commercially prepared resins resulted in the polymerization of the BPACY. Melt mixing was accomplished using a Helicone mixer operating at 280°C with a nitrogen blanket. Mixing time was approximately 3 min. Compression moulding was also carried out at 280°C.

Characterization. Cast films were inspected for optical clarity, which is indicative of single-phase behaviour (except, of course, when the refractive indices of the two components match or when metastability exists due to kinetic factors). The well-dried films and compression moulding were also analysed by d.s.c. Blends were analysed by gel permeation chromatography to ensure that the BPACY had not polymerized. The dynamic mechanical behaviour of the compression moulded BPACY/PXE blend was investigated at temperatures between −150 and 200°C at a frequency of 5 Hz using a Rheometrics RDS spectrometer.

Results

Cast films. Table 1 summarizes the results of the characterization of cast films containing 50 wt% BPACY. All homopolymers on the CED spectrum, from polyformal to Radel poly(phenyl sulfone), gave clear films with the exception of very high molecular weight poly(methyl methacrylate). Each clear film exhibited a single T_g except for 50/50 BPACY/polystyrene (PS). It should be noted that the refractive indices of PS and polycarbonate are nearly identical, which might explain why the BPACY/PS film appears transparent even though two T_gs are observed by d.s.c.

Figure 1 displays the composition dependence of T_g for BPACY/PS as well as BPACY/PXE blends. The

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Table 1 Miscibility of 50/50 blends of BPACY with a spectrum of glassy thermoplastics

Polymer	CED[15] [$\times 10^{-6}$ J m^{-3}]	Optical appearance	Resin T_g (°C)	Blend T_g(s) (°C)
Poly(vinyl cyclohexane) (Lab. prep., M_w=95400, M_w/M_n=1.25)	285	cloudy	140	n.d.
BPA polyformal (i.v.=0.5 dl g^{-1})	318	clear	90	108
Polystyrene (Koppers Co., Dylene 8G, M_w=350000)	339	clear[a]	106	120, 148
Poly(xylylene ether) (i.v.=0.49 dl g^{-1})	339	clear	214	180
Tetramethyl BPA polycarbonate (i.v.=0.57 dl g^{-1})	352	clear	205	179
Poly(methyl methacrylate) (PMMA)				
1. Scientific Polymer Prod., M_w=93000	377	clear	100	127
2. Rohm & Haas Co., M_w=3500000	377	clear/cloudy[b]	110	n.d.
Poly(vinyl acetate) (Aldrich., Cat No. 18948-0; med. MW)	377	clear	31	91
Styrene–acrylonitrile (SAN) copolymers (Lab. preps:				
1. 16% AN, M_w=110000	375	clear	107	124
2. 26% AN, M_w=100000	400	clear	112	125
3. 29% AN, M_w=100000	404	clear	112	125
4. 35% AN, M_w=130000)	418	clear	109	125
Bisphenol chloral polycarbonate (Lab. prep.)	427	clear	170	n.d.
BPA polysulfone (Union Carbide Co., Udel resin)	452	clear	190	n.d.
BPA poly(etherimide) (Lab. prep.)	460	clear	220	n.d.
Poly(ether sulfone) (ICI Victrex, grade 200P)	490	clear	230	178
Poly(phenyl sulfone) (Union Carbide Co., Radel resin)	527	clear	213	177

n.d.=not determined; i.v.=intrinsic viscosity
[a] Film observed to be optically clear (even though calorimetric analysis revealed two T_gs) due to proximity of refractive indices
[b] Cloudiness developed slowly during prolonged drying at elevated temperatures. Although the cause is unknown it may have been due to polymerization of BPACY since BPA polycarbonate and PMMA have limited solubilities

behaviour of the BPACY/PXE system is that which is expected for a completely miscible blend of a high-T_g polymer with a lower-T_g diluent. In contrast, the BPACY/PS system is shown to be only partially miscible. Low concentrations of BPACY (<20 wt%) raise the T_g of the PS. However, at higher concentrations the existence of two T_gs is evidence of phase separation. Further, the phase behaviour of BPACY/PS blends has been found to be quite sensitive to changes in the molecular weight of the PS. A 50/50 blend of BPACY with PS having a molecular weight of 20400 was found to be completely miscible across the entire composition range, while a similar blend with PS with a molecular weight of 31500 displayed two T_gs at BPACY compositions greater than 40 wt%.

Melt mixed blend. Gel permeation chromatography confirmed that no polymerization of the BPACY had

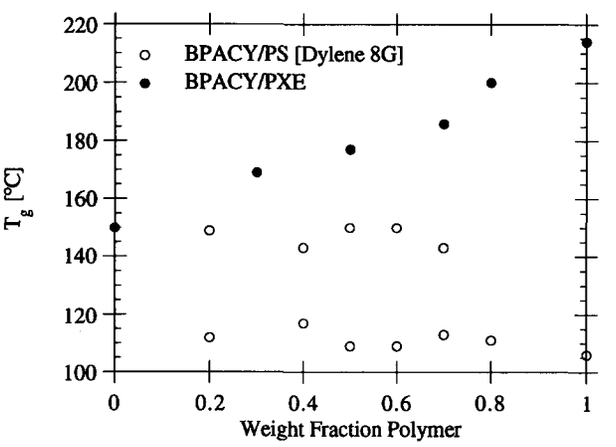

Figure 1 Composition dependence of T_g for BPACY blends

occurred during melt processing. D.s.c., as well as dynamic mechanical thermal analysis, revealed a single T_g for the blend. Dynamic mechanical spectroscopy at 5 Hz revealed the alpha relaxation of the 50/50 BPACY/PXE blend to be 180°C, midway between the T_gs of the BPACY and PXE. This result demonstrates the feasibility of melt processing blends of BPACY with high-T_g thermoplastics without necessarily polymerizing the cyclic oligomers.

Discussion

The spectrum of polymer CEDs in which the BPACY display high levels of solubility is quite large (CED range $\simeq 200 \times 10^6$ J m^{-3}). This range is about as great as the range of CEDs of truly small molecule agents ($M_w < 500$) that have been found to swell each of a series of glassy polymers to at least 20 vol% (CED range $\simeq 370 \times 10^6$ J m^{-2})[7-12]. In contrast, the CED range for miscibility when mixing polymers of high molecular weight is much smaller. For example, when PXE ($M_w = 5000$) is mixed with a series of polymers of moderate to high molecular weight ($M_w > 16\,000$) with varying CEDs[13], the CED range for miscibility is only about 8×10^6 J m^{-3}. Since the densities[14] and chemical structures of BPACY and linear BPA polycarbonate are identical, they will have the same CED (i.e. 385×10^6 J m^{-3})[15].

In the simplest of models, the difference in CEDs between two components of a blend can be used as an estimate of the enthalpy of mixing. Further, the maximum tolerable difference in CEDs for which a blend will remain miscible is a function of the molecular weights of the two species. The higher the molecular weights, the smaller the maximum tolerable difference in CEDs. In this respect, the fact that the BPACY are miscible with polymers spanning a wide range of CEDs may be explained by their relatively low molecular weight. A more rigorous examination of the miscibility behaviour of the BPACY requires a direct comparison to the miscibility behaviour of linear BPA carbonate oligomers. This analysis has been completed[14] and will be the subject of a future paper[16].

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