Physical, Thermomechanical, and Rheological Properties of Bisphenol A–Tetrabromobisphenol A Copolycarbonates

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SYNOPSIS

The physical, thermomechanical, and rheological properties of bisphenol A–tetrabromobisphenol A copolycarbonates (BA–TBBA coPCs) were studied as a function of copolymer composition. TBBA carbonate segments in the copolymer induce proportionally increased glass transition temperatures, heat distortion temperatures, ignition resistance, tensile and flexural moduli, and density. Properties that do not change proportionately with copolymer composition are coefficient of linear thermal expansion, ambient notched Izod and dart puncture impact strengths, and refractive index. Many properties of BA-TBBA coPCs, including glass transition temperature, heat distortion temperature under load, and modulus, approach those of amorphous high-performance thermoplastics such as polyetherimide and polyethersulfone. However, these copolymers have the possible advantage of melt blending with bisphenol A polycarbonate to form homogeneous alloys with variable and controllable properties. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Bisphenol A–tetrabromobisphenol A copolycarbonates (BA–TBBA coPCs) are well-known ignition resistance additives for bisphenol A polycarbonate (BA PC) engineering thermoplastic.[1,2] Other properties of these copolymers have not been reported, perhaps due in part to the relatively low thermal stability of the early versions of these materials. A recently reported improved interfacial process for the preparation of BA–TBBA coPCs produces these copolymers with high end-group selectivity and good thermal stability. Unlike the solution process, the one-step interfacial phosgenation of mixtures of BA and TBBA forms, after coupling of the intermediate oligomers, single-phase segmented block copolymers having relatively short block lengths (4–9 units in the 1 : 1 coPC).[3,4] The improved thermal stability of the BA–TBBA coPCs made by this process is due to high chain end capping efficiency, which gives low concentrations of phenolic end groups, and to the absence of a tertiary amine catalyst side reaction with the chloroformate-terminated oligomers to

form carbamate end groups.[5,6] Other studies on the side reaction of tertiary amines with chloroformates of brominated phenols have recently appeared.[7] The BA–TBBA coPCs made by this new process withstand extrusion, compression molding, and injection molding at temperatures up to 320°C without degradation, thereby facilitating a full evaluation of their properties. This report provides an overview of the physical, thermomechanical, and rheological properties of these copolymers and the relationship of these properties to copolymer composition.

EXPERIMENTAL

Materials

BA–TBBA coPCs were prepared by the previously described interfacial polycondensation process.[3,4] Phenol or p-t-butylphenol (PTBP) were used as chain terminators. A 10 MFR BA PC (CALIBRE brand 300-10), $M_w = 28,900$ g/mol, was used for comparative analyses.

Molding

Test specimens were either compression molded on a Tetrahedron MTP-14 compression molder at

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307°C and 40 kpsig or injection molded on an Arburg 70 ton injection molding machine at 315°C. Specimen geometries are noted for each analysis.

Analytical

Gel permeation chromatography (GPC) analyses were done as previously described.[4] Differential scanning chromatography (DSC) analyses were performed on a DuPont Instruments 910 differential scanning calorimeter using DuPont Instruments Thermal Analyst 2100 software. Glass transition temperatures (T_g) were recorded at a 20°C/min heating rate under nitrogen and are reported as the inflection point of the heat flow curve. The distortion temperature under load (DTUL) at 264 psi was determined in accordance with ASTM D-648-72 on a Tinius Olsen heat distortion tester. Coefficients of linear thermal expansion (CLTE) were measured on a DuPont Model 943 thermomechanical analyzer using DuPont Instruments Thermal Analyst 2100 software. Cell calibration gave a cell constant of 1.12. Samples of $10 \times 5 \times 3.2$ mm approximate dimensions were cut from compression-molded plaques. Rough edges were sanded smooth before analysis. Thermal gravimetric analysis (TGA) was performed on a DuPont Instruments 951 thermogravimetric analyzer using Thermal Analyst 2100 Software. A single pellet of the material ($\sim$ 8 mg) was equilibrated at 80°C and then heated at 100°C/min to 500°C. Air was purged through the cell during the analysis. Limiting oxygen indices (LOI) were performed according to ASTM A-2863-87. UL-94 ignition resistance testing was performed in accordance to ASTM D-4804-88 on 3.2-mm injection or compression molded bars.

Tensile experiments were performed on microtensile bars (ASTM D-638, type V) using a MTS 50 kpsi servo-hydraulic test frame at room temperature with a constant displacement rate of 5.08 mm/min. Local strain measurements were recorded using a micro-extensiometer, gauge = 3.05 mm and full scale = 0.24 mm (8%), attached to the sample. Flexural moduli were recorded on an Instron Model 1130 test frame according to ASTM D-790. Izod impact data at 23°C were obtained in accordance with ASTM D-256-72A on a TMI pendulum testing machine. Dart impact testing was carried out on injection molded 6.35-cm diameter disks on a Dynatup Model 8000 impact instrument using a 1.6-mm diameter tup attached to a 59-kg hammer. The hammer was dropped from a 30.48 cm height to attain a velocity of 2.39–2.44 m/s. This method is similar (but not identical) to ASTM D-3763-84.

Refractive indices were obtained in accordance with ASTM D-542-50 on an ABBE instrument at 25°C, standardized with the glass standard (n_s = 1.5128) versus α-bromonaphthalene contact liquid. Optical properties (YI, % transmittance, and % haze) were determined on a Hunter Lab Colorimeter Model D-25-9 instrument using method ASTM D-1925. Density was estimated by water volume displacement of compression-molded samples.

Rheology data were obtained on an Instron Model 3211 capillary rheometer. Barrel temperature was set at 306°C providing a melt temperature of 300 ± 5°C. Samples were dried under vacuum at 70°C for at least 18 h and conditioned at temperature under pressure in the barrel for 7 min prior to analysis.

RESULTS AND DISCUSSION

BA–TBBA coPCs having various molar ratios of comonomers, from 4 : 1 to 1 : 1, were prepared by the previously reported improved interfacial process.[3,4] The molecular weights of these copolymers, as determined by GPC, are in the ranges expected for the amount of monophenol chain terminator employed in the synthesis (Table I). The level of terminator used was adjusted in order to produce coPCs above their apparent critical molecular weight.[4] The properties described below were measured on compression-molded or injection-molded coPC samples and are summarized in Table II.

Thermal Properties

The glass transition temperature (T_g) of BA–TBBA coPCs varies linearly with composition between the T_g's of the respective homopolymers (BA PC = 155°C, TBBA PC = 265°C; Table III). Although these copolymers have segmented block sequence architectures,[3,4] only single T_g's were observed by DSC. The T_g of copolymers generally follows the

Table I BA–TBBA CoPC Compositions and GPC Molecular Weights

BA/TBBA	Monophenol (%)	M_w	M_n	Disp
1 : 1	Phenol (2)	57,133	18,794	3.04
55 : 45	Phenol (3)	35,257	11,398	3.09
3 : 2	Phenol (3)	22,465	8,007	2.81
2 : 1	PTBP (3)	32,208	13,739	2.34
3 : 1	PTBP (3)	42,859	12,302	3.48
4 : 1	PTBP (3)	29,604	11,060	2.68

Table II   BA–TBBA CoPC Properties[a]

Property	BA–TBBA Molar Ratios			
	1 : 1	2 : 1	4 : 1	BA PC
T_g (°C)	210 (2)	195 (2)	177 (2)	155 (2)
DTUL (°C @ 1.82 MPa, $\frac{1}{8}$ in.)				
Compression molded	188 (2)	177 (2)	163 (2)	—
Injection molded	—	157 (2)	145 (2)	131 (2)
CLTE (ppm/°C)	—	63 (1)	65 (1)	72 (1)
T_d (°C, air)	380 (2)	410 (2)	410 (2)	410 (2)
LOI	> 60	> 60	60	27
UL-94 ($\frac{1}{8}$ in.)	—	V-0	V-0	V-2
Tensile modulus (MPa)	2628 (76)	2580 (61)	2343 (28)	1992 (30)
Tensile strength (MPa)				
Yield	89 (1)	88 (1)	77 (1)	61 (1)
Ultimate	86 (1)	61 (4)	54 (2)	52 (5)
Elongation at yield (%)	15.1 (1.4)	16.5 (.33)	15.3 (.22)	13.7 (.22)
Elongation at break (%)	16 (2)	20 (2)	33 (4)	142 (37)
Flexural modulus (MPa)	3276 (83)	2650 (102)	2421 (61)	2200 (55)
Notched Izod impact (J/m)	80.1 (5)	106.8 (5)	106.8 (5)	849 (5)
Dart impact:				
Max. force (Mdyne)	—	25.2 (3)	27.2 (3)	24.3 (3)
Energy to break (J)	—	59.7 (6)	81.3 (8)	71.9 (8)
Density (g/cm³)	1.82 (.02)	1.50 (.02)	1.35 (.02)	1.20 (.02)
Refractive index	—	1.593	1.593	1.585
Yellowness index	6	6	3	1

[a] Average deviations are noted in parentheses.

Gordon–Taylor relationship[8] [Eq. (1)], where K is an empirical constant and W is the indicated co-monomer mole fraction. Observed T_g's follow the linear rule of mixtures[8] [Eq. (2)], which follows from Eq. (1) with $K = 1$, rather than the Fox equation[9] [Eq. (3)], which was devised for random copolymers and which approximates Eq. (1) with $K = 2$ (Fig. 1). That the relationship between T_g and copolymer composition reduces to the linear

$$T_g = \frac{T_{g,\text{BA}} + (KT_{g,\text{TBBA}} - T_{g,\text{BA}})W_{\text{TBBA}}}{1 + (K - 1)W_{\text{TBBA}}} \quad (1)$$

$$T_g = T_{g,\text{BA}}W_{\text{BA}} + T_{g,\text{TBBA}}W_{\text{TBBA}} \quad (2)$$

$$1/T_g = W_{\text{BA}}/T_{g,\text{BA}} + W_{\text{TBBA}}/T_{g,\text{TBBA}} \quad (3)$$

form is not unexpected with these relatively similar and apparently miscible short block segments.

Table III   BA–TBBA CoPC Observed and Calculation T_g's

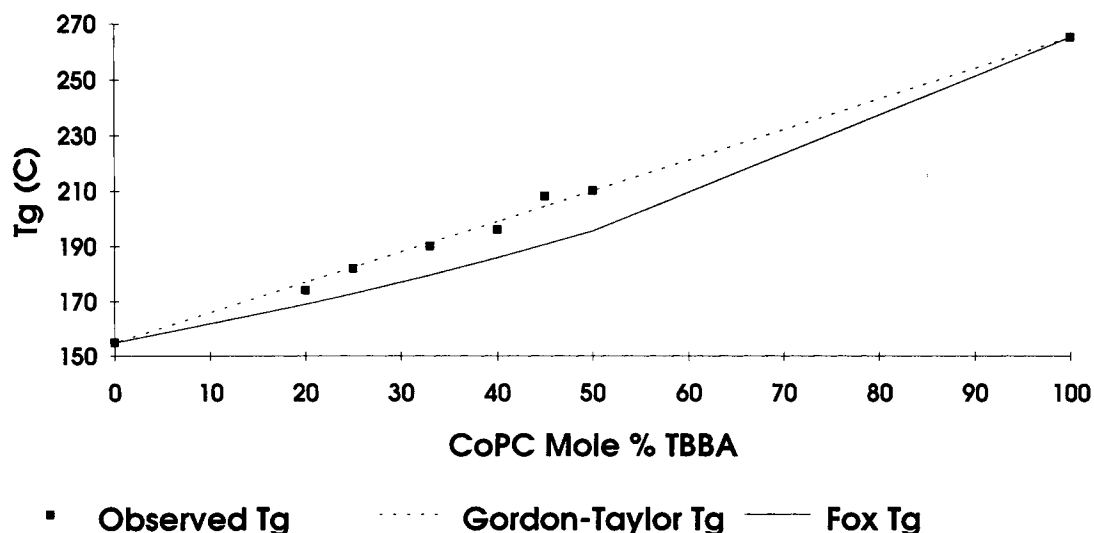| BA–TBBA	Mol % BA	Mol % TBBA	T_g (°C)	Gordon–Taylor[a]	Fox
0 : 1	0	100	265	265	265
1 : 1	50	50	210	210	196
55 : 45	55	45	208	205	191
3 : 2	60	40	196	199	186
2 : 1	67	33	190	191	180
3 : 1	75	25	182	183	173
4 : 1	80	20	174	177	169
1 : 0	100	0	155	155	155

[a] $K = 1$ in Eq. (1).

Figure 1 T_g vs. mol % TBBA in BA-TBBA CoPCs.

The deflection temperature under load (DTUL) of BA–TBBA coPCs ranges from about 145 to 190°C and varies expectedly with composition, but is dependent on sample melt processing and heat history. The DTUL of compression-molded coPCs were found to be about 20°C higher than injection-molded samples. Annealing of injection-molded samples produced the higher DTUL values of the compression-molded specimens. This behavior is attributed to relaxation of residual stress induced by injection molding, which is relieved upon annealing. The DTUL of compression molded copolymers increases about 1°C per mol % TBBA in the copolymer.

The coefficient of linear thermal expansion (CLTE) of BA–TBBA coPCs is about 10% lower than that of BA PC, but does not change much with composition. These CLTE differences correspond roughly to those of the flexural modulus, an expected trend since both of these properties depend inversely on polymer molar volume.[10] Compression-molded and annealed injection-molded samples gave slightly higher CLTE results than unannealed injection-molded specimens.

Thermal gravimetric analysis (TGA) of the three copolymers in air shows a gradual weight loss similar to that of BA PC. The temperature at 5% weight loss (T_d) is decreased only for the 1 : 1 BA–TBBA coPC. While the cause of this difference coPC stability was not determined, it is likely that HBr generated by coPC thermal decomposition can auto-catalyze subsequent degradation reactions, thereby lowering T_d, but this effect is only observed for coPCs having very high amounts of bromine where HBr is generated faster than it is swept away from the polymer by the air flow through the apparatus.

Ignition Resistance

The limiting oxygen index (LOI) of BA–TBBA coPCs is very high due to the high concentration of bromine in the copolymers. The LOI of the 2 : 1 and 1 : 1 coPCs could only be estimated as much greater than 60 due to equipment limitations. The UL-94 rating of 2 : 1 and 4 : 1 coPCs is V-0 for both $\frac{1}{8}$- and $\frac{1}{16}$-in. specimens. The high bromine content in these copolymers imparts very short burn times and the concomitant lack of dripping in these specimens compared to BA PC.

Mechanical Properties

Room temperature tensile measurements show proportional increases in tensile modulus and yield strength in BA–TBBA coPCs with increasing TBBA content in the copolymer. Tensile moduli up to 2600 MPa and yield strengths up to 89 MPa were found, increases of about 12 and 0.5 MPa per mol % TBBA, respectively, from the values for BA PC to the 2 : 1 coPC. Proportionate increases in tensile properties are not observed with increasing TBBA content beyond the 2 : 1 copolymer. Because the tensile measurements were performed on compression-molded, type V specimens, the ultimate properties of these copolymers (break strength and elongation) found in this study are largely dominated by specimen flaws and should not be taken as material parameters. In particular, strain hardening is not observed
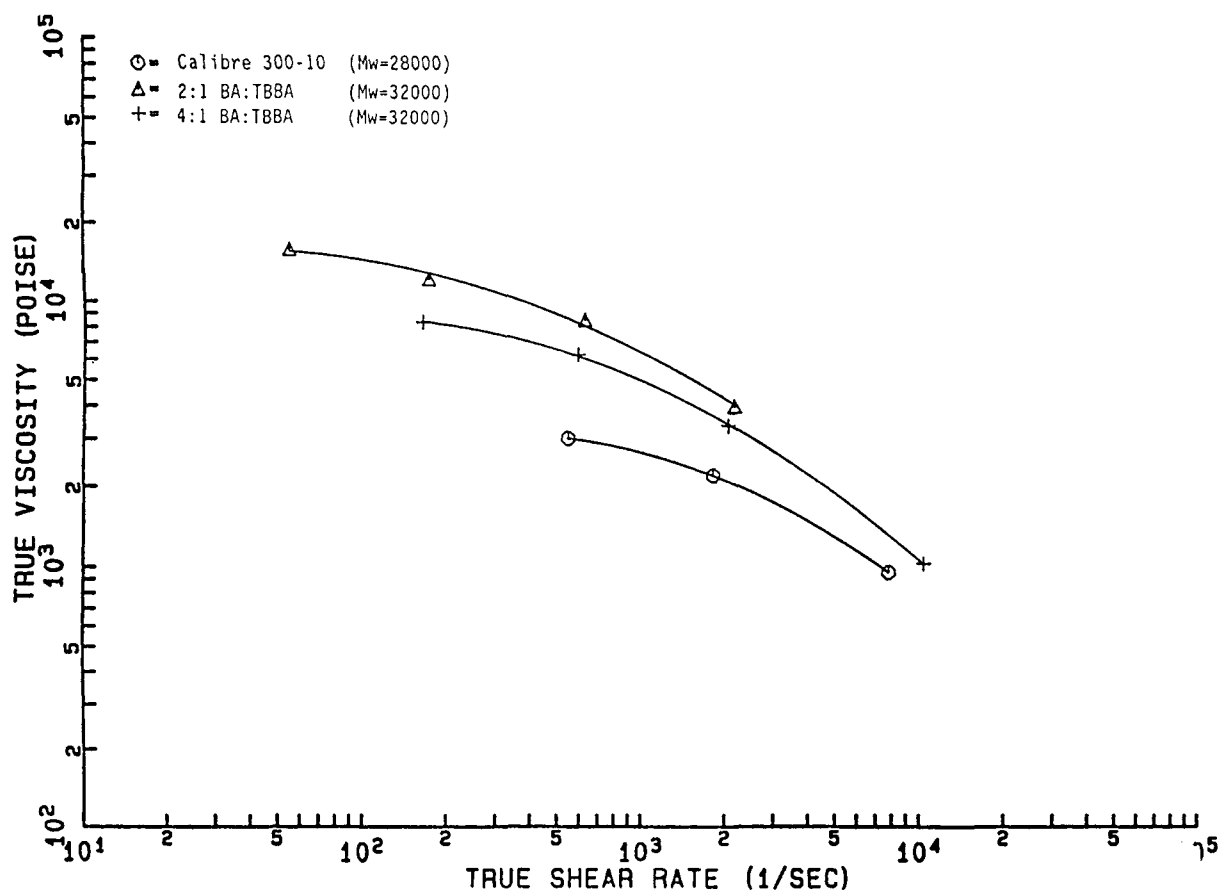
Figure 2 Capillary melt viscosities of BA-TBBA CoPCs and BA PC.

in any of the samples (and is expected for BA PC). The failure mechanism (ductile or brittle) was observed to be dependent on coPC composition and molecular weight, with low TBBA content and high molecular weight favoring ductile failure.

The flexural moduli of BA–TBBA coPCs increase substantially with increasing TBBA content. The 1 : 1 coPC has almost a 50% higher flexural modulus than BA PC.

BA–TBBA coPCs are notch-sensitive polymers but have a high puncture impact resistance. Notched Izod impact strengths for the 4 : 1 and 2 : 1 BA–TBBA coPCs are ∼ 80–110 J/m at room temperature, compared to BA PC's value of ∼ 850 J/m. Conversely, dart punction impact testing shows that the brominated copolymers withstand puncture impact as well as BA PC at room temperature. The 2 : 1 coPC has a somewhat lower maximum force and energy to break than both the 4 : 1 coPC and BA PC; however, a higher molecular weight 2 : 1 coPC might reverse this trend. The disparity in the results of these two modes of impact testing suggests that the BA–TBBA coPCs are near their ductile-

brittle temperature transition for notched Izod impact strength.

The density of BA–TBBA coPCs increases sharply with TBBA content, with the density of the 1 : 1 coPC about 1.5 times that of BA PC. Density is one of several material properties, along with modulus, CLTE, solubility parameter, and cohesive energy density, which is inversely proportional to polymer molar volume.[10] It is therefore surprising that density scales with modulus over the full range of coPC compositions examined, but CLTE does not.

Optical Properties

BA–TBBA coPCs have significantly higher refractive indices (RI) than BA PC. The RI of the 2 : 1 and 4 : 1 copolymers were found to be the same within experimental error and about 0.5% greater than the RI of BA PC.

Injection molding of 2 : 1 and 4 : 1 BA–TBBA coPCs at about 300°C produced good optical quality samples with yellowness index (YI) ranging from 3 to 6, transmission of about 90%, and haze less than

1%. Tinting with Violet B produced samples having YI less than 1, transmission greater than 86%, and haze less than 1%.

Rheological Properties

Figure 2 shows the capillary melt viscosities of 2 : 1 and 4 : 1 BA–TBBA coPCs and of BA PC at 300°C. The melt viscosities of the 28,000 M_w BA PC and the 32,000 M_w 4 : 1 BA–TBBA coPC are very similar at high shear rates (10,000/s) even though they differ greatly at lower shear rates (100–1000/s). This indicates a higher sensitivity to shear for the copolymers and accounts for the easier than expected injection molding (based on its T_g) of the 4 : 1 BA–TBBA coPC.

CONCLUSIONS

Many of the physical, thermomechanical, and rheological properties of BA–TBBA coPCs expectedly vary as a function of copolymer composition, but several of these properties are relatively constant over the range of compositions examined. TBBA carbonate segments in the copolymer induce proportionally increased glass transition temperatures, heat distortion temperatures, ignition resistance, tensile and flexural moduli, and density. Properties that do not change in proportion to copolymer composition are CLTE, notched Izod and dart puncture impact strengths, and refractive index.

Glass transition temperatures and heat distortion temperatures up to 210 and 188°C, respectively, are found for coPCs with as much as 50 mol % TBBA. CoPC thermal stability is about the same as BA PC as shown by TGA. The high bromine content in these copolymers results in high ignition resistance ratings.

These copolymers have relatively low notched Izod impact strengths compared to BA PC. Brittle fractures are observed at room temperature, thus the ductile-brittle temperature transition of these copolymers is above room temperature. Puncture impact strength at room temperature ($\frac{1}{8}$ in. thickness), a more practical impact property in many applications, of these coPCs is invariant with composition and is equal to or greater than that of BA

PC. CoPC optical properties are very good, making them possible candidates for high-temperature lighting applications.

Many properties of BA–TBBA coPCs, including T_g, DTUL, and modulus approach, those of amorphous high-performance thermoplastics such as polyetherimide and polyethersulfone. However, these copolymers have the possible advantage of melt blending with BA PC to form homogeneous alloys with variable and controllable properties.

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