Structural and Thermal Behavior of PC/PBT Blends

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SYNOPSIS

Blends of polycarbonate (PC) with poly(butylene terphthalate) (PBT) were characterized using density measurements, DSC, IR, and TGA. Addition of PBT increases the density values of blends linearly. All the blends show a single glass transition temperature, indicating the miscibility of the two polymers in the amorphous phase. With more than 6% addition of PBT to PC, PBT crystallizes as per its own crystal structure. The addition of 4% PBT to PC improves the thermal stability at higher temperature than does pure PC. IR studies shows that addition of PBT improves the intermolecular forces in PC, in particular, on the endgroup and the $C-CH_3$ and $C=O$ groups as indicated in the frequencies 1020, 1370, and 1770–1790 cm^{-1}. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blending is a new approach for the preparation of materials. Polyblends are physical mixtures of structurally different polymers with no covalent bonds occurring between them. The constituent polymers adhere together through the action of secondary bond forces only. The degree of compatibility is one of the major factors in determining the system's final properties. The other controlling factors include chemical composition, polymer crystal structure, morphology, molecular weight, and processing. The advantages of this approach over developing a new polymer is that polymer blending is quicker and more economical. A completely homogeneous polyblend tends to average the properties of the two polymers composing the polyblend, in direct proportion to the volume or weight fraction of each polymer. Sometimes, some degree of incompatibility leads to a superior balance of useful properties.[1] Such blends have been the subject of several reviews.[2–9] Most of the investigations discuss phase morphology changes and the properties of the polyblends.[10–23]

A compatible polyblend exhibits mechanical properties proportional to the ratio of the constituent of the blend, where incompatibility often leads to a material with poor mechanical properties. Generally, the incompatible nature of polymers can be converted into an advantageous situation if proper care is taken in preparing and processing the polymers.

Polycarbonate (PC) is a noncrystalline amorphous and thermoplastic polymer. Of all the amorphous polymers, it has exceptional properties like good impact strength, ductility, extreme toughness, transparency, resistance to burning, and maintenance of useful engineering properties over a temperature range of −200°C to +140°C. However, the shortcomings of PC are (1) high melt viscosity, creating difficulties in processing, (2) high impact strength for household purposes, (3) high glass transition temperature, and (4) a slow rate of crystallization. Several properties of PC can be improved by blending it with miscible polymers.[24–28]

Poly(butylene terephthalate) (PBT) is a highly crystallizable thermoplastic polyester having good mechanical and electrical properties, excellent solvent resistance, and good hydrolytic stability.[24] The crystallizable characteristics of PBT may improve some of the properties of PC.

This article deals with the structural and thermal properties of the PC/PBT blend, where the weight percentage of PBT is restricted to 10%.

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EXPERIMENTAL

Preparation of the Blends

The polymers used were all commercial polymers. Blended films were produced by solution casting. The solvent chosen here is chlorobenzene for PC and phenol for PBT.

DSC Studies

DSC studies were done on a delta series DSC7 system from ambient temperature to 300°C at a heating rate of 20°C/min. The primary thermograms were obtained as heat flow against temperature.

Density Measurement

Density of pure PC and PC/PBT films were measured in a density gradient column by means of carbon tetrachloride (density: 1.595 g/cc) and xylene (density: 0.855 g/cc). The range of the density used in this experiment was 1.10–1.40 g/cc.

TGA Studies

TGA studies were done on a Mettler TA 3000 system in a dynamic atmosphere of oxygen-free nitrogen from ambient temperature to 760°C at a heating rate of 5°C/min. The primary thermograms were
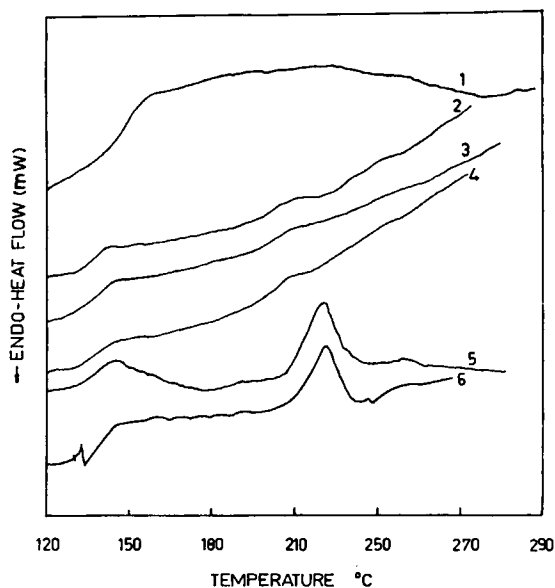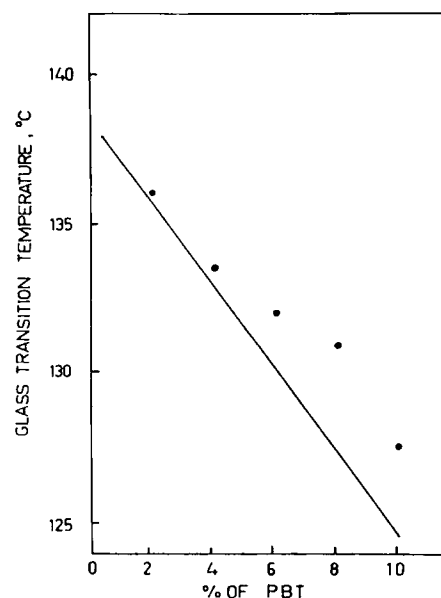

Figure 2 T_g's for various PC/PBT compositions derived from the Fox equation (continuous line) and experimental values.

obtained from TGA traces as the residual weight in percentage against temperature.

IR Studies

IR spectra were taken for PC and PC/PBT blends in a Perkin-Elmer IR 577 spectrophotometer. The instrument was calibrated against polystyrene. The film was directly exposed to an IR beam for the spectra.

RESULTS AND DISCUSSION

DSC thermograms of PC/PBT blends are shown in Figure 1. Pure PC and all the blends exhibit a single, composition-dependent glass transition. The glass transition temperatures are shown in Figure 2. The glass transition temperatures calculated theoretically by the Fox equation[29] are indicated by a continuous line. Pure PC has a glass transition temperature at 138.8°C. PC is an amorphous and stiff polymer. So, the glass transition temperature is high and there is no melting endotherm.[26,30] On the other hand, PBT is a flexible polymer, whose T_g is 30°C.[24] PC/PBT blends show glass transition temperatures lower than that of pure PC. All the blends show a single glass transition temperature, indicating miscibility of the two polymers in the amorphous phase.

Figure 1 DSC thermograms for (1) 100/0, (2) 98/2, (3) 96/4, (4) 94/6, (5) 92/8, and (6) 90/10 PC/PBT blends.

To study the effect of miscibility, the Fox equation was applied and it is compared with the experimental value. The observed value is found to be lesser than the calculated values in all the compositions. This may be attributed to the fact that as PBT becomes crystallized in the blend, its concentration in the amorphous phase of the blend is reduced. As a result, the observed glass transition temperatures deviates from that expected theoretically. The blends having more than 6% PBT show a melting endotherm in the range of 220–222°C. This indicates that PBT crystallizes as per its own crystal structure when the weight percentage is more than 6%.

The melting point of PBT is reported as 232°C.[24] This indicates that the melting point observed is comparatively low. This may be because of the low crystal size of PBT. The blends having up to 6% PBT shows that the heat flow continuously increases above glass transition temperature with respect to temperature. This indicates that some sort of crystallization is induced in DSC.

The density of pure PC is 1.198 g/cc. In general, PC is an amorphous polymer. The density value of 1.200 g/cc is reported for this polymer.[24] This indicates that the polymer is in an amorphous phase only. Addition of PBT increases the density value of blends linearly. PBT is a semicrystalline polymer. The percentage of PBT used in this work is restricted to 10%. The two-phase model is put forward
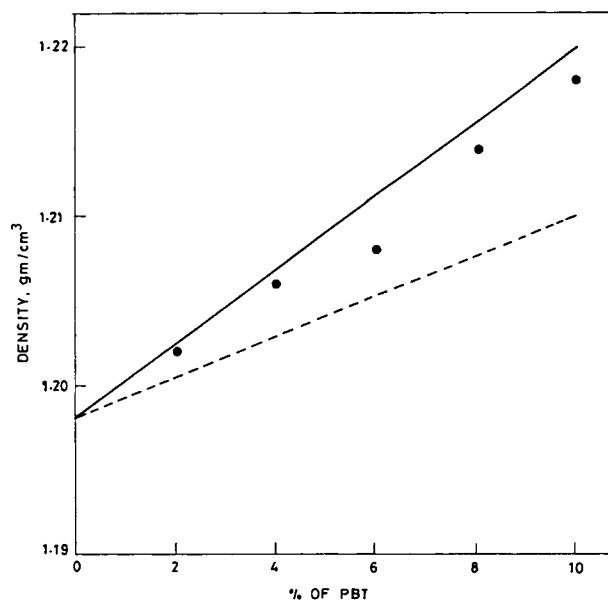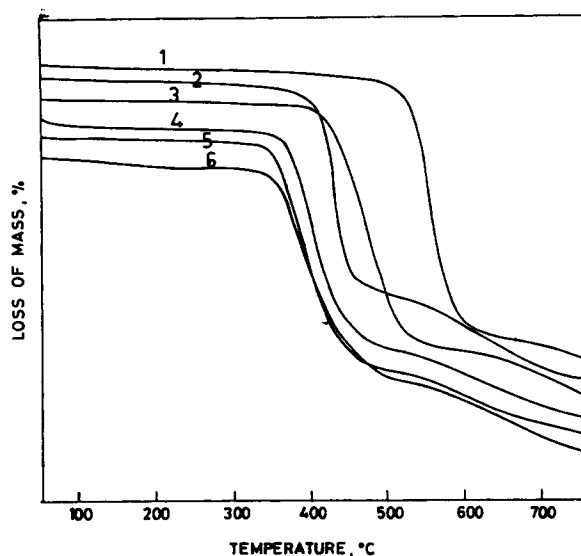

Figure 4   TGA thermograms for (1) 100%, (2) 98/2, (3) 96/4, (4) 94/6, (5) 92/8, and (6) 90/10.

to calculate the density of blends using the rule of mixtures with a constant maximum packing fraction of the phases and continuity of the phases. The resultant density of the blends can be calculated as follows:

$$db = W_1 d_1 + W_2 d_2$$

where W is the weight fraction, and d, the density. 1 refers to PC and 2 refers to PBT. In Figure 3, the calculated values of the density of the blended films as shown by the lines assuming that PBT is in (a) purely amorphous and (b) purely crystalline form. The crystalline density and amorphous density values of PBT are taken as 1.396 and 1.280 g/cc, respectively.[24] However, PBT does not crystallize in the blends of 100/0 to 94/6 PC/PBT. So, in this range, a higher density may be possible due to (1) higher interaction between the two components, leading to higher packing, and/or (2) including some sort of crystallization in PC, thereby increasing the relative density of PC.

The TGA and DTG thermograms obtained from pure PC and PC/PBT blends are shown in Figures 4 and 5, respectively. Table I shows the IDT, TD_{max}, IPDT, and percentage weight loss of these blends. Table II shows the activation energy for the decomposition in the temperature range of 300–600°C.

Pure PC shows two-phase decompositions at the temperatures 266 and 534°C with a weight loss of 74 and 6%, respectively. This indicates that the majority of the decomposition takes place at around
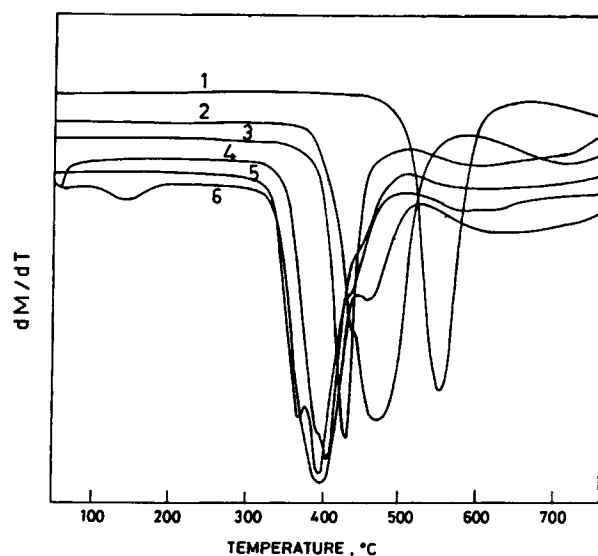

Figure 3   Theoretical and experimental density values of PC/PBT blends (———) 100% crystalline and (- - -) 100% amorphous.

Figure 5 DTG thermograms for (1) 100/0, (2) 98/2, (3) 96/4, (4) 94/6, (5) 92/8, and (6) 90/10 PC/PBT blends.

392°C in the temperature range of 266–432°C. The 98/2 PC/PBT blend shows a single-phase decomposition with 100% weight loss at 371°C. Also, addition of 2% PBT to PC decreases the value of the IDT and TD_{max} values. It shows that the blend decomposes at slightly lower temperature than does pure PC and that thermal stability also is reduced.

The 96/4 PC/PBT blend shows a different trend. The IDT, TD_{max}, and IPDT values are higher than those of the 98/2 PC/PBT blend. Addition of 4% PBT to PC improves the thermal stability at higher temperature than does pure PC. It can be noted that the IDT value of this blend is appreciably higher than are the melting points of PBT.

For blends having more than 4% PBT, IDT, TD_{max}, and IPDT values decrease linearly with increase in PBT content. The decrease in IDT values

Table II Activation Energy of Pure Polycarbonate and Its Blends

Sample	Activation Energy (kcal/mol)		
PC:PBT	Phase I	Phase II	Phase III
100:0	—	15	56
98:2	—	12	—
96:4	—	9	20
94:6	—	8	29
92:8	—	23	23
90:10	0.3	8	27

are expected and can be attributed to the introduction of more flexible butyl groups, which makes the chain more prone to degradation at lower temperature.

The 90/10 PC/PBT blend shows a three-phase decomposition step. Because of overlapping of two different decomposition regions, the corresponding mass fraction could not be estimated. Decomposition at 90°C shows the presence of moisture due to a higher percentage of PBT.

The spectrum obtained from pure PC and PC/PBT blends are shown in Figure 6. Table III shows the vibrational frequency of pure PC and its characteristic assignment. The behavior of the characteristic bands of PC/PBT blends are tabulated in Table IV. The bands associated with various ring vibration modes of PC are 1610, 1510, 1400, 880, and 760 cm^{-1}. Stretching vibrations of $C-CH_3$ in PC occurs at 2990 cm^{-1}; the 1250 cm^{-1} band is a conformational band indicating the presence of $-O-C-O-$ linkage. These stretching band vibrations remain unchanged in all the blends. The $C-H$ bending vibration of CH_3 at 1370 cm^{-1} in pure PC is not present in the PC/PBT blends.

Table I IDT, TD_{max}, % of Weight Loss, and IPDT Values of Pure PC and Its Blends

	Phase I				Phase II				Phase III			
Sample	IDT (°C)	TD_{max} (°C)	Wt. Loss %	IPDT (°C)	IDT (°C)	TD_{max} (°C)	Wt. Loss %	IPDT (°C)	IDT (°C)	TD_{max} (°C)	Wt. Loss %	IPDT (°C)
1	—	—	—	—	266	432	74	392	534	614	6	650
2	—	—	—	—	256	428	100	371	—	—	—	—
3	—	—	—	—	316	440	74	426	550	719	14	629
4	—	—	—	—	278	412	73	286	526	620	23	643
5	—	—	—	—	250	410	74	271	528	616	21	643
6	90	144	3	127	276	398	73	270	526	616	24	616

The C — H bending frequency of the ring in plane occurs at 1510 cm^{-1} in pure PC and it remains unchanged with addition of 2% PBT. On the other hand, with addition of more than 4% PBT, there is a slight shift of bands toward lower frequency. The C — H bending frequency ring out of plane at 760 cm^{-1} also shows similar behavior. All these observations indicate that addition of PBT hinders the C — H intermolecular interaction.

In case of pure PC as well as blends containing less than 4% PBT, the C = O stretching frequency of a nonconjugated system occurs at 1770–1790 cm^{-1}. This indicates that addition of more than 4% PBT improves the uniformity of the vibrations which concentrates at 1780 cm^{-1}. Also, addition of 4% PBT in PC modifies the C = O bending vibrations from 840 to 830 cm^{-1}. The C — OH stretching frequency occurring at 1020 cm^{-1} indicates cyclic alcohol, which is the endgroup of PC. Addition of PBT changes this vibration to 1010 cm^{-1}, indicating action of intermolecular forces on the endgroup.

CONCLUSIONS

1. Addition of up to 10% PBT in PC reduces the T_g of PC from 138.8 to 127.5°C, indicating miscibility between the two polymers in the amorphous phase.
2. Addition of up to 6% PBT induces a higher interaction between two components and in-

Table III   Absorbtion Assignment for Pure Polycarbonate Film

Assignment	Wavenumber (cm^{-1})
C — H stretching vibration of C — CH$_3$	2990
C = O stretching frequency of nonconjugated system	1770–1790
C — C stretching frequency of ring C — C	1610
C — H stretching frequency of ring in plane	1510
C — C stretching frequency of ring in plane	1400
C — H bending vibration of CH$_3$	1370
Characteristic for — O — C — O —	1150–1250
C — O stretching frequency of secondary cyclic alcohol (endgroup of PC)	1020
C — O stretching frequency of ester	1080
C — C — C stretching frequency of ring	880
C = bending frequency out of plane	840
C — H bending frequency ring out of plane	760
C = O in plane bending	550

creases the density values. The presence of PBT hinders the C — H bending frequency at 1510 and 760 cm^{-1}, the C = O bending vi-
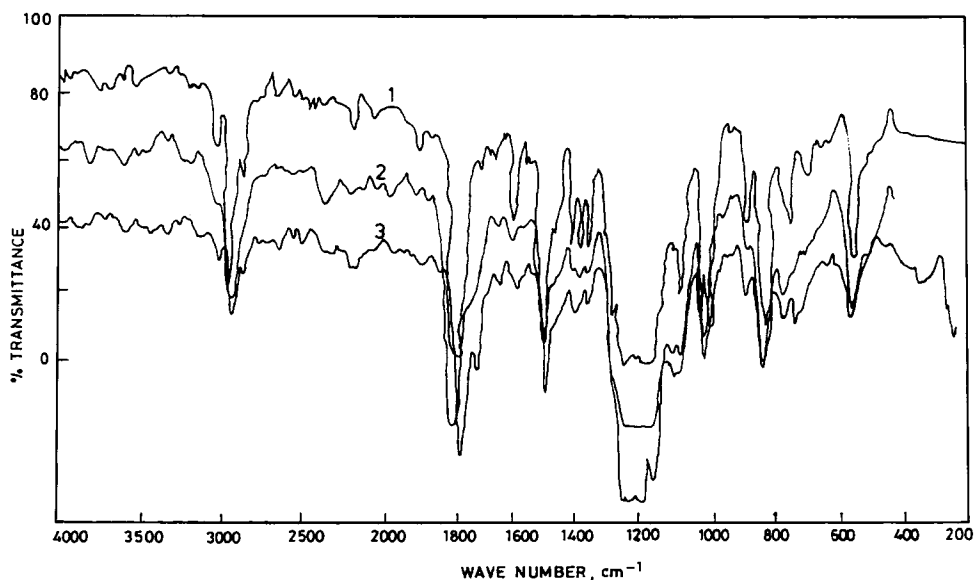

Figure 6   IR spectra for (1) 100/0, (2) 96/4, and (3) 90/10 PC/PBT blends.

Table IV IR Absorption Assignment for PC/PBT Blend Films

Assignment	96/4 Blend (cm^{-1})	90/10 Blend (cm^{-1})
C—H stretching vibration of C—CH_3	2970	2990
C=O stretching frequency of nonconjugated system	1770–1790	1780
C—C stretching frequency of ring C—C	—	—
C—H bending frequency of ring in plane	1500	1500
C—C bending frequency of ring in plane	—	—
C—H bending vibration of CH_3	—	—
Characteristic for —O—C—O—	1160–1290	1160–1260
C—O stretching frequency of ester	—	—
C—OH stretching frequency of secondary cyclic alcohol (endgroup of PC)	1010	1010
C=O bending frequency ring out of plane	820	830
C=H bending frequency ring out of plane	—	—
C=O in plane bending	550	550

bration at 840 cm^{-1}, and the C—OH stretching frequency at 1010 cm^{-1}.

3. The PBT phase segregates and crystallizes in the PC/PBT blend when the weight percent is more than 6%.

4. Addition of 4% PBT to PC improves the thermal stability of the blends with higher IDT, TD_{max}, and IPDT values.

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