Miscibility of Poly(1,4-Cyclohexamethylene Terephthalate) Blends with Polyarylate

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ABSTRACT: The miscibility of poly(1,4-cyclohexamethylene terephthalate) (PCT) having an aliphatic cyclic segment blended with Polyarylate (PAR) was investigated by means of calorimetric measurements. It was found that all the PCT/PAR blends are miscible and show a single, composition-dependent glass transition temperature (T_g). The T_g composition dependence has been analyzed by using the Gordon–Taylor equation and the values of T_g obtained experimentally agree quite well with those calculated theoretically by using that equation. Also, the melting point depression phenomenon that occurred in miscible polymer pairs was observed up to 40 wt % PCT content. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1947–1949, 2000

Key words: poly(1,4-cyclohexamethylene terephthalate); polyarylate; miscibility; blend; Gordon–Taylor equation

INTRODUCTION

The miscibility behavior of polymer–polymer blends has been investigated for more than 30 years for scientific and industrial interests.[1,2] For high-molecular weight polymers, the free energy of favorable mixing is primarily dominated by an exothermic heat of mixing since entropic contributions are so small in such systems. Specific intermolecular interaction such as hydrogen-bond formation, *n–n* complex formation, and a variety of other specific interactions are responsible for the exothermic heat of mixing.[3–5]

Poly(1,4-cyclohexamethylene terephthalate) (PCT) is a thermoplastic engineering plastic with good physical properties, especially good thermal resistance. This polymer is commercially available for various extrusion applications under the name Kodel that was made by division of East-

man Kodak Co. and has been described in part by a number of publications.[6] But it has a disadvantage of molecular weight decrease caused by thermal decomposition that occurs during polymerization as well as processing at high temperature.[7] To overcome this disadvantage, many researches have been attempted to blend with other polymers.[8,9]

In this short article, we report the miscibility of poly(1,4-cyclohexamethylene terephthalate) with polyarylate (PAR), amorphous aromatic polyester made from bisphenol-A and isophthalic/terephthalic acids, which has excellent mechanical and flammability properties.[10] The techniques employed include differential scanning calorimetry (DSC) for glass transition and melting behaviors.

EXPERIMENTAL

PCT was obtained from Eastman Kodak Co. and its inherent viscosity is evaluated as 0.9 dL/g using the Cannon-Fenske type viscometer in the 1,1,2,2-tetrachloroethane/phenol (4 : 6 v/v) at 25°C. PAR (Unitika Co. U-100; $M_n = 21,200$ $M_w = 51,400$) used in this study is based on bisphenol-A and isophthalic and terephthalic acid (in

the mole ratio of isophthalic acid/terephthalic acid = 50/50).

Blends of PCT/PAR were made by the solution precipitation method of Kimura et al.[11] PCT and PAR were dissolved in 1,1,2,2-tetrachloroethane/ phenol (4 : 6 v/v) cosolvent and the solution mixture was precipitated in tenfold methanol. The precipitated powder was washed with hot methanol several times and dried in a vacuum oven for 2 days at 100°C. The weight fractions of PCT/PAR blends are 80/20, 60/40, 40/60, and 20/80.

The calorimetric characterization studies were carried out using a Perkin-Elmer, DSC-7. The heating rate was 20°C/min and calibration of the instrument was carried out using high purity indium and zinc.

RESULTS AND DISCUSSION

To observe miscibility behavior between PCT and PAR, after a first scan up to 320°C to provide the same thermal history for all sample, followed by rapid quenching to −60°C, the DSC curves were recorded at a heating rate of 20°C/min. The glass transition temperature was taken as the inflection point of the specific heat increment. The PCT/ PAR blends were characterized by only single glass transition temperatures (T_gs) that were dependent on the composition of the blends and intermediates between those of PCT (94.3°C) and PAR (193.5°C).
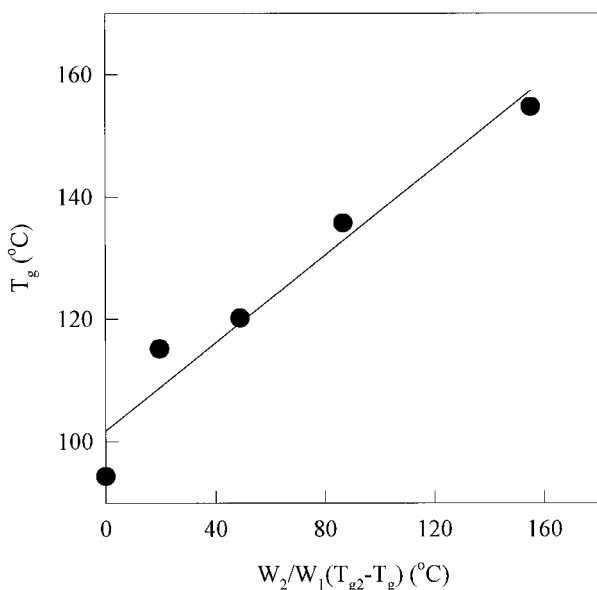
Figure 1 Gordon–Taylor plot of T_g data from PCT/ PAR blends.
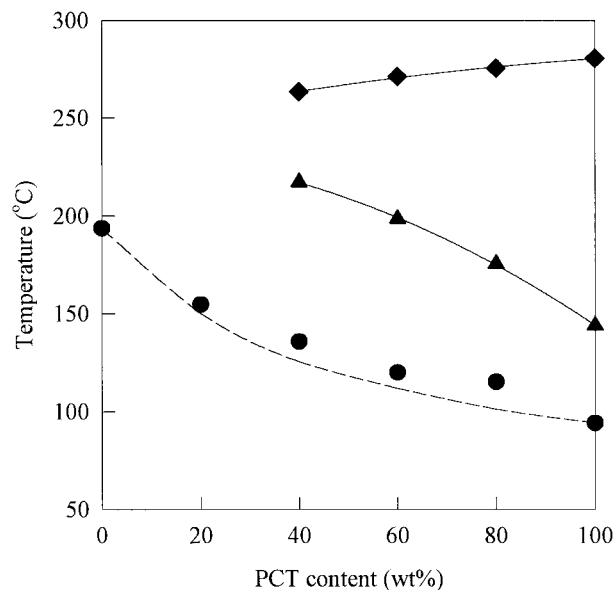
Figure 2 Transition behavior of PCT/PAR blends. The broken line was calculated from the Gordon–Taylor equation with k = 0.359; (●) T_g, (◆) T_m, (▲) T_c.

The several theoretical and empirical equations have been used to describe the T_g-composition dependence of miscible blend systems. One of those, the Gordon–Taylor equation,[12] can be written as follows:

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

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} are the glass transition temperatures of components 1 and 2, respectively, w_1 and w_2 are the weight fraction of component 1 and 2 respectively, and k is a constant. It has been suggested that the value of k relates to the strength of interaction between the components in the blends, although no theoretical basis for such a relationship has been suggested. Figure 1 shows a plot of this relationship for the PCT/PAR blend, which gives k = 0.359. Higher the value of k, higher is the interaction between polymer pair. In this system, the value of k for miscible polymer pair has lower than other miscible polymer pair that has strong interaction such as hydrogen bonding. The positive deviation from Gordon–Taylor equation at high PCT content (80 wt %) is caused from the crystallization of PCT in the blend during the quenching. A similar phenomenon has been observed for other miscible crystalline/amorphous blend system.[13,14] As shown in Figure 2, the values of T_g obtained experimentally agree quite well with those calcu-

**Table I   Thermal Characteristics
of PCT/PAR Blends**

PCT/PAR Blend Ratio	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_f (J/g)
100/0	94.3	143.8	280.5	45.8
80/20	115.1	175.4	275.4	30.8
60/40	120.1	198.4	271.1	10.5
40/60	135.7	217.1	263.3	1.8
20/80	154.7	ND[a]	ND	ND
0/100	193.5	ND	ND	ND

[a] ND: not detected.

lated theoretically by using the Gordon–Taylor equation. The results strongly suggest that PCT and PAR are miscible in the melt and in the amorphous state.

A melting temperature depression phenomenon is characteristic of the miscible blends. When one component is crystalline and the other is non-crystalline, a melting point depression of the crystalline phase is taken as an additional evidence of the miscibility.[15,16] Table I shows the melting points of the PCT/PAR blend systems. The melting temperature of blend samples decreases from 280.5 to 263.3°C as the PAR content increases to 60 wt %. From the glass transition temperature and melting point depression, we can concluded that PCT interacts with PAR, that is, PCT is miscible with PAR. Table I also shows that the crystallization temperature (T_c) of the quenched samples is the functions of blend composition. It can be seen that T_c increases with increasing in PAR content, indicating that the crystallization of PCT in the blend becomes progressively more difficult with increasing PAR content. The blend with 80 wt % or more PAR content did not have any crystallization exotherm. By measuring the areas under the melting peaks, it should be possible to evaluate the heat of fusion. The results obtained (Table I) imply that the crystallinity of PCT in the blend greatly decreases with increasing PAR content, which supports the idea that PAR is completely miscible with PCT over the entire composition range in the melt. The decrease in the crystallinity of PCT with increasing PAR content is due to an increasing T_g of the system.

In summary, PCT exhibits miscibility with PAR. The existence of a single, composition-dependent T_g and melting temperature depression phenomenon reveal that the blend forms a homogeneous single phase at melt state. Adding PAR to PCT greatly lowers the crystallinity owing to an increasing T_g of the blend system.

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