

Phase Behavior of Blends Containing Amorphous Poly(resorcinol phthalate-*block*-carbonate) and Semicrystalline Polyesters

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ABSTRACT: The phase behavior of poly(resorcinol phthalate-*block*-carbonate) (RPC) with engineering polyesters was investigated by using differential scanning calorimeter (DSC) and dynamic mechanical analysis. RPC was found to form miscible blends with poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(cyclohexylmethylene terephthalate) (PCT), but was partially miscible with poly(1,4-cyclohexanedimethylene-1,4-cyclohexanedicarboxylate) (PCCD) in the melt state and below the melting temperature (T_m). The degree of

melting-point depression indicates that the RPC is most miscible with PCT followed by PET and then PBT. Furthermore, with the help of empirical DSC data and the Nishi-Wang equation, the interaction parameters between RPC and PET, PBT, and PCT were quantified to be -0.36 , -0.33 , and -0.54 , respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2623–2633, 2008

Key words: polyesters; copolymer of resorcinol and carbonate; melting-point depression

INTRODUCTION

Engineering plastics have been widely used due to their excellent mechanical properties and high maximum use temperatures. Engineering thermoplastics are commonly used in automotive and telecommunication outdoor applications. In these applications, engineering thermoplastics are expected to meet long-term UV-resistance requirements. This is often achieved by adding a UV agent as an additive. However, UV additives tend to migrate to the surface and, as a result, might be extracted when the polymer is exposed to certain chemicals. In addition, UV additives tend to degrade over time and do not protect the polymer matrix during the course of its expected lifetime. In contrast, some engineering plastics inherently have robust UV stability due to their chemical structure. UV-resistant engineering plastics can either be used as is or in a polymer blend to overcome the migration issue. However, the effectiveness of the UV-resistant polymer in the blends can be dramatically different from a miscible blend versus an immiscible blend due to a difference in the blend morphology. Therefore, it is critical to understand the miscibility of the UV-resistant polymers with other polymers.

The present study investigates the phase behavior of the blends of poly(resorcinol phthalate-*block*-car-

bonate) (RPC) with engineering polyesters. The RPC in this study consists of iso- and terephthalate esters of resorcinol (RPC) and bisphenol-A polycarbonate. The polyesters involved in this study were poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), poly(cyclohexylmethylene terephthalate) (PCT), and poly(1,4-cyclohexanedimethylene-1,4-cyclohexanedicarboxylate) (PCCD).

RPC is relatively less known to the polymer industry. Based on the limited literature^{1,2} available, excellent physical properties, chemical resistance, and UV resistance properties have been reported. It has also been reported that RPC is miscible with polyetherimide³ and has formed useful blends with polycarbonate.⁴

Semicrystalline polyesters such as PET, PBT, PCT, and PCCD were chosen, as they are representative engineering polyesters in practical applications. The four polyesters were also chosen to investigate the effect of the structure of the dialcohol and the diester on the phase behavior of the blends.

In the past, other types of polyarylate and their blends with good mechanical and UV-resistance properties have been studied.^{5–11} Huo and Cebe⁷ reported for the first time that the melting point of PBT was depressed in the blend with a polyarylate based on bisphenol A and isophthalic acid. Blends of semicrystalline PBT and certain amorphous polyarylates have an attractive interaction in the entire composition range by virtue of a negative Flory interaction parameter (χ).

The phase behavior was studied using glass transition temperature and melting-point depression

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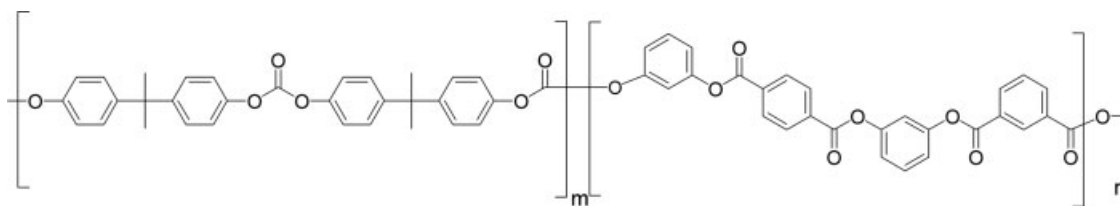


Figure 1 Poly(resorcinol phthalate-*block*-carbonate).

measurements, and optical observation at various annealing temperatures and compositions. The samples in this study were prepared by extrusion or extrusion followed by molding to simulate blend properties in practical applications.

EXPERIMENTAL

Materials

The PBT sample was obtained from SABIC Innovative Plastic Co. (formerly GE Plastics) and its weight-average molecular weight was 107,000 g/mol against polystyrene standards by gel permeation chromatography (GPC). The PET sample was obtained from DuPont Chemical Co., and its weight-average molecular weight was 88,000 g/mol against polystyrene standards. The PCT sample was obtained from Eastman Chemical Co., and its weight-average molecular weight was 70,000 g/mol against polystyrene standards. The PCCD sample was obtained from Eastman Chemical Company, and its weight-average molecular weight was 80,400 g/mol against polystyrene standards.

RPC was from Sabic Innovative Plastics Co., and its weight-average molecular weight was 25,000 g/mol against polycarbonate standards in GPC. The synthetic scheme has been published elsewhere.¹ The polymer (RPC80) was a multi-block copolymer with 20 mol % of BPA-based carbonate repeating units and 80 mol % of resorcinol phthalate repeating units (Fig. 1). In the resorcinol phthalate block, 1/1 mol ratio of isophthalic and terephthalic acids was used.

The polymer pellets with stabilizers of Sandostab P-EPQ and mono zinc phosphate³ were extruded on a 28-mm Werner Pfleiderer Twin Screw Extruder with a vacuum-vented mixing screw, at a barrel and die head temperature between 250 and 270°C and 150–300 rpm screw speed. The extruder has eight independent feeders and could be operated at a maximum of 30 kg/h. The extrudate was cooled through a water bath prior to pelletizing. Test parts were injection molded on a van Dorn molding machine with a set temperature of ~ 250 and 270°C. The pellets were dried for 3–4 h at 60–120°C in a forced air-circulating oven prior to injection molding. For dynamic mechanical analysis and differential scanning calorimetry (DSC), Izod parts were molded in

dimensions of 63.5-mm length, 12.7-mm width, and 3.2-mm thickness.

Measurements

Differential scanning calorimetry

Thermal transitions, including the glass transition temperatures, the melt and crystallization temperatures, and the enthalpies of melting and crystallization of the blends were carried out on a differential scanning calorimeter (DSC) (TA Instruments Model Q1000). High purity indium and lead were used as standards for temperature calibration, and indium was also used as the standard for heat flow calibration. All the samples were subjected to heating, cooling, and heating cycles at 20°C/min.

Extensive studies^{12–18} have shown that transesterification may occur in polymer blends containing ester and carbonate functional groups in melt processes, which would affect the phase behavior of the blends. To avoid confounding of results by transesterification, for this study, it was ensured that the experimental conditions were optimized to minimize transesterification. Following the method used by Huo and Cebe⁷ and Liau et al.,⁹ these blends containing 60% ester were chosen to determine if transesterification would indeed occur under the experimental conditions. Samples were heated up to a maximum temperature of 280°C for blends containing PBT, PET, and PCCD and, at 310°C, for RPC/PCT blends. At high temperatures, the samples were held for different periods of time, ranging from 1 to 10 min, and this was followed by a cooling and heating cycle. Changes in both the temperature and the enthalpy of melting were evaluated to determine the possible occurrence of transesterification or material degradation. For blends of RPC with PBT and PCCD at 280°C, and with PCT at 310°C, the isothermal scan for durations of up to 10 min showed no substantial effect on either the melting temperature or the enthalpy, thereby suggesting no occurrence of significant transesterification or material degradation at the holding temperatures. However, for RPC/PET blends, a remarkable decrease in both the melting temperature and the melting enthalpy was observed as the isothermal time at 280°C increased from 1 to 3 min, indicating the occurrence of transesterifica-

tion. To minimize the effect of transesterification and simultaneously remove the thermal history, a holding time of 1 min at 280°C was used for RPC and PET blends. For the other blends, the same holding time at the high end temperature was used.

Dynamic mechanical analysis

Dynamic mechanical properties of those blends were performed with a TA instrument, TA 2980 or TA Q800. The blends were molded into Izod bars to fit into a dual cantilever fixture. A small amplitude flexural deformation with a frequency of 1 Hz and a temperature scan from room temperature to the melting point at a ramp rate of 3°C/min were used. Phase behavior was also investigated by DMA after the samples were annealed at 140, 165, and 190°C for 24 h.

RESULTS

The miscibility of the blend of RPC and polyesters was investigated by using various methods including optical clarity of extruded pellets and molded parts, DMA, and DSC. To investigate the processing effects, some samples were extruded and other samples were molded after extrusion.

Miscibility in melt state

Optical clarity and a single-component dependent T_g are considered to be signatures of miscibility of amorphous polymer blends.^{19–23} For blends of amorphous polymers and semicrystalline polymers, optical clarity can also be used as a quick-test method to determine miscibility in the melt state.

The blends of RPC80 with PET, PBT, or PCT were extruded at various compositions for studying the phase diagram of the blends. To evaluate the phase diagrams of the blends at temperatures higher than the melting point of the polyesters, the optical clarity of the blend was investigated as a function of temperature in the melt state.²⁴ Samples with 20, 40, 60, and 80 wt % RPC80 were put on a hot plate at a heating rate of ~50°C/min. All the samples became optically transparent upon reaching the melting temperature of the blends. The samples were heated up to 450°C where all formed a dark brown to black color, typical indication of degradation. Between 250 and 450°C, all the polyester blends remained transparent in the melt state. It is an indication that RPC is miscible with PET, PBT, or PCT at all compositions in the melt state in the temperature range of 250–450°C. Further quantitative studies were done with DSC and DMA.

Glass transition temperature of the blends

The phase behavior of the blends was examined by using both DMA and DSC measurements. Figure 2(b)

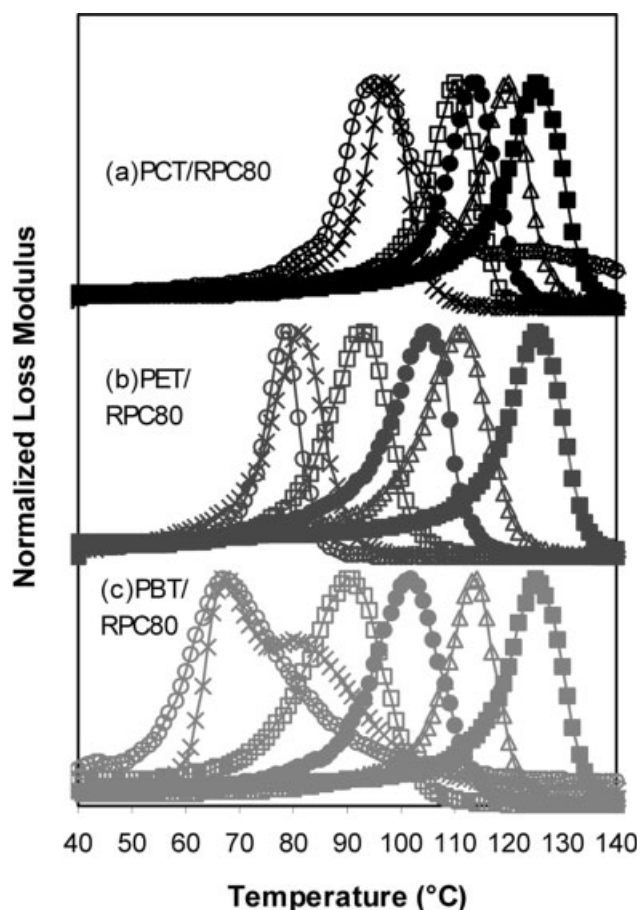


Figure 2 DMA curves of RPC80 blends with (a) PCT, (b) PET, or (c) PBT (○: 100% PCT (a), PET (b), or PBT (c), ×: 20% RPC80, □: 40% RPC80, ●: 60% RPC80, △: 80% RPC80, and ■: 100% RPC80).

shows the loss modulus of the blends of PET and RPC80. The peak maximum was used to determine the glass transition temperature. DMA curves show a single T_g at all compositions with increasing peak temperatures at higher amounts of RPC80, indicating that the blends are miscible. Figure 2(a,c) shows PBT and PCT blends with RPC80, respectively. None of the blends displayed two distinct glass transition temperatures. Some samples, e.g., 80% PBT, had a second peak that is attributed to crystallization upon heating of the samples, as verified from the presence of an exothermic peak in a DSC scan. A single T_g at all compositions indicates that PET, PBT, and PCT are miscible with RPC80 in the amorphous phases.

In Figure 3, the glass transition temperatures of the blends were plotted against the Fox equation²⁵ to examine if the experimental T_g data can be correlated to theoretical prediction for a miscible blend.

$$\frac{1}{T_{g,\text{blend}}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

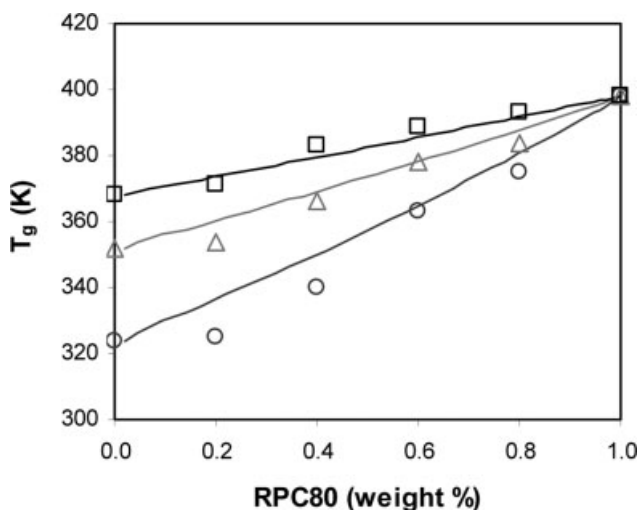


Figure 3 Glass transition temperature of RPC80 blends by using DMA (\square : PCT, \triangle : PET, and \circ : PBT). Samples were given as molded.

where w_1 and w_2 are weight fractions of Polymers 1 and 2, respectively.

Good agreement was obtained between the experimental T_g and predicted T_g . This indicates that PET,

PBT, and PCT are miscible with RPC80 in the amorphous phases.

DSC results confirm the findings from the DMA measurements for the entire composition range; RPC80 forms miscible blends with PBT, PET, or PCT. Figure 4 shows a single T_g for the three blend systems. Again, changes of T_g with the composition conform well with those of Fox prediction, as illustrated in Figure 5. It should be noted that the amorphous composition was corrected to account for the crystalline phase in the blends before Fox's equation was used, although the correction did not make a significant difference for blends containing 40% or 20% polyesters. The correction was based on the polyester crystallinity estimated from the DSC measurements (refer Table I for further details). For the blend containing 60% PCT, a broad transition covering $\sim 30^\circ\text{C}$ was observed as shown in Figure 4. Annealing this blend at elevated temperatures did not induce a remarkable change in the shape of the transition. It is noticed that this broadness is only observed in the second heat scan and not in the first. Note that the sample in the second scan had much higher crystallinity than that in the first scan. The sample in the first scan still had the thermal

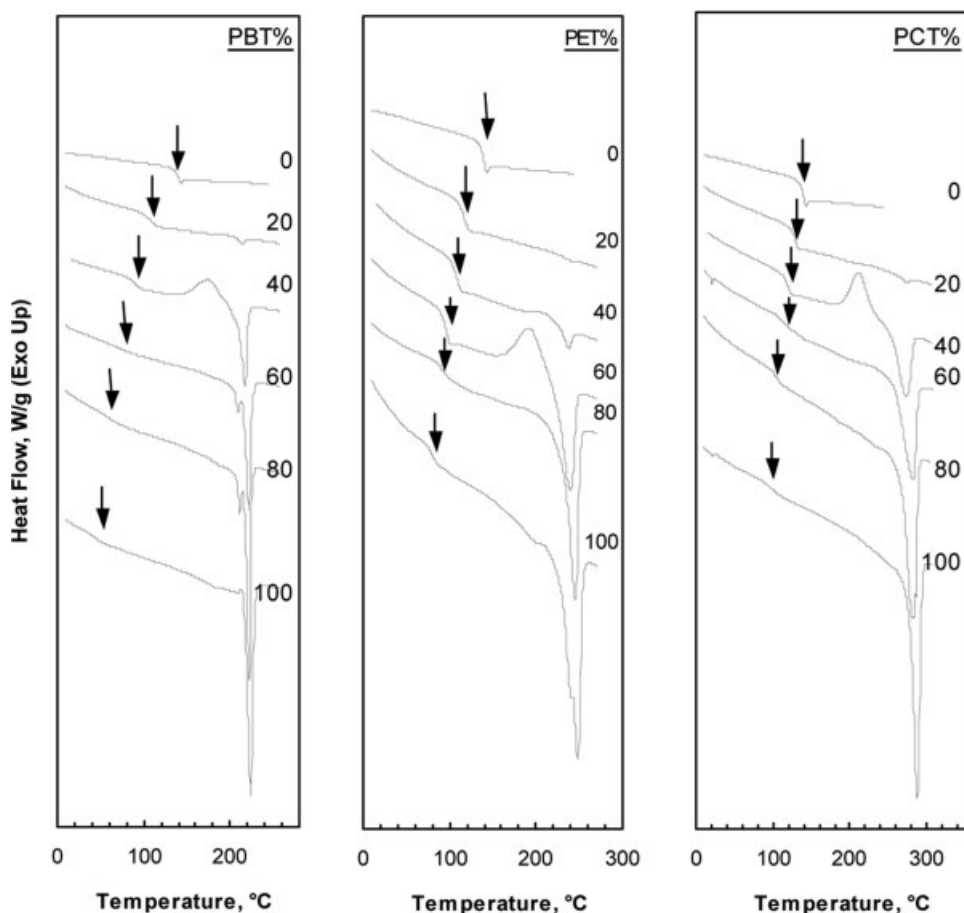


Figure 4 DSC traces of RPC, PBT, PET, PCT, and the indicated blends. Arrows indicate glass transition temperatures. The curves are arbitrarily shifted vertically to improve clarity.

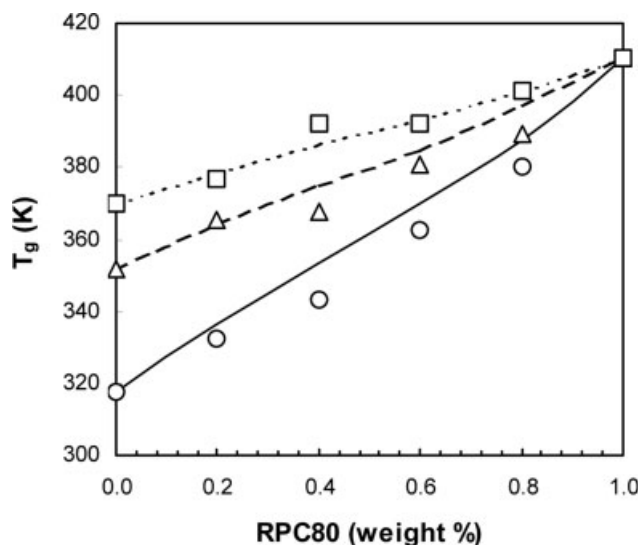


Figure 5 Glass transition temperature of RPC80 blends by using DSC (\square : PCT, \triangle : PET, and \circ : PBT). The solid line, the long-, and the short-dashed lines are T_g s of Fox prediction for RPC80/PBT, RPC80/PET, and RPC80/PCT blends, respectively. Note: Fox prediction was based on the corrected amorphous composition.

history of being quenched from the extruded melt and showed the occurrence of crystallization above the T_g . In contrast, the sample in second scan was slowly cooled from the melt and had enough time to fully develop crystallinity upon cooling. Therefore, the higher

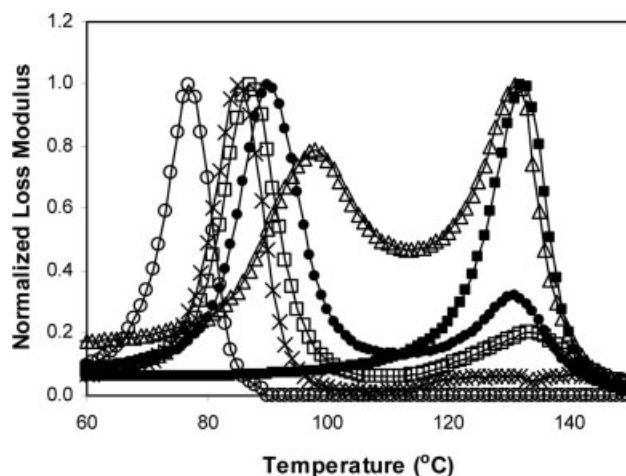


Figure 6 DMA curves of PCCD and RPC80 blends. (\circ : 100% PCCD, \times : 80% PCCD, \square : 60% PCCD, \bullet : 40% PCCD, \triangle : 20% PCCD, and \blacksquare : 100% RPC80).

crystallinity of PCT may contribute to the broadness of T_g in the second heat due to the existence of compositional heterogeneity,^{26,27} or specifically, a rigid amorphous phase²⁸ for this blend, which is also discussed in detail later.

In Figures 6 and 7, the blend of PCCD and RPC80 had two distinct glass transition temperatures at all compositions in DMA and DSC. However, the shift of the glass transition temperature in the blends indicated the partial miscibility of the components.

TABLE I
DSC Results of RPC80 Blends Containing PBT, PET, and PCT

RPC80 blends	T_g ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH_c (J/g)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	$(\Delta H_m - \Delta H_c)/\Delta H_f^{\circ}$ ^a	Corrected RPC80 in amorphous phase, wt. fraction ^b	T_g from Fox equation ($^{\circ}\text{C}$)
RPC80/PBT	0/100			223.9	42.9	0.29	0.00	44.5
	20/80			222.1	34.8	0.23	0.25	63.1
	40/60			221.7	27.3	0.18	0.45	80.3
	60/40	175.0	13.4	217.4	17.4	0.12	0.63	97.0
	80/20			214.3	0.771	0.01	0.80	114.5
	100/0					0	1.00	137.0
RPC80/PET	0/100			248.2	37.3	0.29	0.00	78.7
	20/80			245.1	28.0	0.22	0.24	91.2
	40/60	193.1	14.2	239.2	18.6	0.14	0.44	102.0
	60/40	209.6	1.52	237.3	2.21	0.02	0.60	111.8
	80/20			237.0	0.271	0.002	0.80	123.9
	100/0					0	1.00	137.0
RPC80/PCT	0/100			287.6	37.6	0.19	0.00	96.8
	20/80			281.9	33.1	0.17	0.23	105.3
	40/60			282.5	24.2	0.12	0.43	113.1
	60/40	212.1	12.5	273.2	15.8	0.02	0.60	120.1
	80/20	233.4	0.39	274.0	0.811	0.002	0.80	128.3
	100/0					0	1.00	137.0

T_c , peak temperature of recrystallization; ΔH_c , exothermic heat of recrystallization; T_m , peak temperature of melting; ΔH_m , endothermic heat of melting.

^aEstimates of crystallinity in the blends; ΔH_f° , heats of fusion for 100% crystalline polyesters, 150 J/g, 130 J/g, and 199 J/g³⁸ for PBT, PET, and PCT respectively.

^bRPC80 weight fraction in the amorphous phase was corrected by taking into account the polyester crystallinity, i.e., (RPC80 wt fraction in the blends)/[RPC80 wt fraction in the blends + (polyester wt fraction) \times (1-polyester crystallinity)].

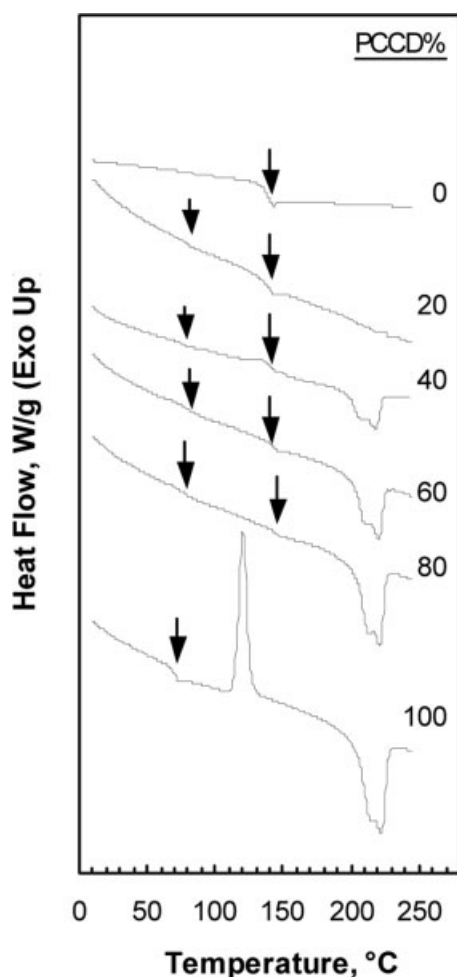


Figure 7 DSC traces of RPC, PCCD, and the indicated blends. The curves are arbitrarily shifted vertically to improve clarity.

Table II summarizes DSC and DMA data on the RPC80/PCCD blends. In DSC, the T_g of PCCD increased at higher concentration of RPC80, and the T_g of RPC80 increased at higher concentration of PCCD. In DMA, the T_g increase of PCCD showed similar trend as in DSC, but the T_g of RPC80 was not substantially increased at higher concentration of PCCD. To investigate the effect of thermal history, the DMA parts were heat aged for 1 day at 190°C followed by DMA testing on the parts. The heat aging was expected to induce crystallinity of PCCD, and as a result, the DMA sample was expected to have similar crystallinity to the DSC sample in the second scan. In addition, heat aging should facilitate diffusion of polymer chains between separated phases. After heat aging, the T_g of RPC80 in DMA confirmed the trend observed in the DSC, an increase in T_g at a higher concentration of RPC80. The shift of the glass transition temperature in the blends indicated the partial miscibility of the components. However, it should be noted that glass transi-

tion temperature of RPC80 in the blend does not agree with a typical trend in partially miscible blends. In a partially miscible blend of a high T_g polymer (H) and low T_g polymer (L), T_g of H is expected to be lower than that of pure H. Further investigation is warranted to understand why the T_g of RPC80 (H in the present system) in the blends is higher than that of pure RPC80. One possible reason could be related to the molecular weight distribution and the nature of the block copolymer. PC that is one of the blocks in RPC80 is miscible with PCCD as reported earlier.^{29–33} As a result, RPC80 polymer chains with low molecular weight could be under strong driving force to move to PCCD phase. The selective removal of low molecular weight RPC80 from RPC80 phase should result in increasing T_g of RPC80 phase, because low molecular polymers are expected to have a lower T_g than higher molecular weight polymers.

The glass transition temperature, the crystallization enthalpy, the melting temperature and enthalpy, and the calculations for all the blends are summarized in Tables I and III.

Phase behavior above T_g

The phase behavior of the blend of PCT and PRC80 was investigated above the T_g of RPC80. Samples were annealed at 140, 165, and 190°C for a period of time ranging from 1 to 24 h. Annealing was not performed at a temperature higher than 190°C, because some samples formed small bubbles in the test specimen at this temperature. Samples annealed at 140°C (slightly above the T_g of RPC80) showed a single T_g at all compositions. In Figure 8, samples annealed at 190°C for 1 h showed very similar DMA curves to the samples annealed at 140°C. Samples were also annealed at 190°C for 1 day. Even the longer anneal-

TABLE II
Glass Transition Temperatures of RPC80 Blends with PCCD by DSC and DMA

RPC80/PCCD (wt/wt)	DSC		DMA on as molded parts		DMA on heat aged parts	
	$T_{g,1}$	$T_{g,2}$	$T_{g,1}$	$T_{g,2}$	$T_{g,1}$	$T_{g,2}$
0/100	70.6		77		86	
20/80	74.5	144.2	85	n.a.	92	139
40/60	78.3	142.6	87	134	96	138
60/40	77.4	n.a. ^a	90	131	100	137
80/20	80.4	137.5	98	131	108	130
100/0		137.0		132		132 ^b

$T_{g,1}$, glass transition temperature of the amorphous PCCD phases; $T_{g,2}$, glass transition temperature of the RPC80 phases.

^aNot available.

^bAnnealed at 140°C for 1 day.

TABLE III
DSC Results of RPC80/PCCD Blends

RPC80/PCCD Blends wt fraction %	$T_{g,1}^a$ (°C)	$T_{g,2}^b$ (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0/100	70.60		120.40	18.18	221.94	22.40
20/80	74.53	144.23			221.20	17.57
40/60	78.28	142.56			219.92	13.13
60/40	77.35	n.a. ^c	136.19	1.57	217.75	9.19
80/20	80.38	137.53			215.88	0.60
100/0		137.06				

^a Glass transition temperatures of the amorphous PCCD phases.

^b Glass transition temperatures of the RPC80 phases.

^c Not available.

ing time of 24 h did not substantially change the DMA curves with the difference in T_g being less than 3°C when compared with the shorter times of annealing (1 h).

The annealing effect on the blends of PCT and RPC80, PET and RPC80, and PBT and RPC80 blends is summarized in Figure 9. All the aforementioned three blend systems showed a single T_g at annealing temperatures from 140 to 190°C, indicating that they are all miscible within the temperature range. It is worthy to note that the annealing caused a shift in the glass transition temperatures to higher temperatures and broadening of the peaks. The degree of the shift and broadening of the T_g , however, did not depend on the annealing temperatures. The peak broadening and shift are attributed to higher crystallinity upon annealing because the crystallization is expected to increase the amount of interfacial area between the amorphous and crystalline phases. The reduced mobility at the interfacial area should increase the T_g of the polymer and the coexistence of

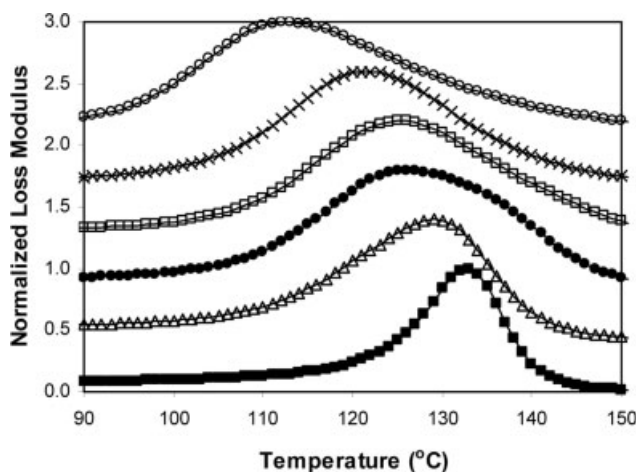


Figure 8 DMA curves of PCT and RPC80 blend after samples except 100% RPC80, which were annealed at 190°C for 1 h. RPC80 sample (100%) was annealed at 140°C for 1 day because 190°C is higher than T_g of the material. (○: 100% PCT, ×: 80% PCT, □: 60% PCT, ●: 40% PCT, △: 20% PCT, and ■: 100% RPC80). The curves are normalized and shifted to y-axis.

polymer chains in the amorphous phase and interface should increase the heterogeneity of the T_g , i.e., broadening the T_g peak. The effect of crystalline phase on shifting and broadening of the T_g has been also discussed in the literature.²⁸

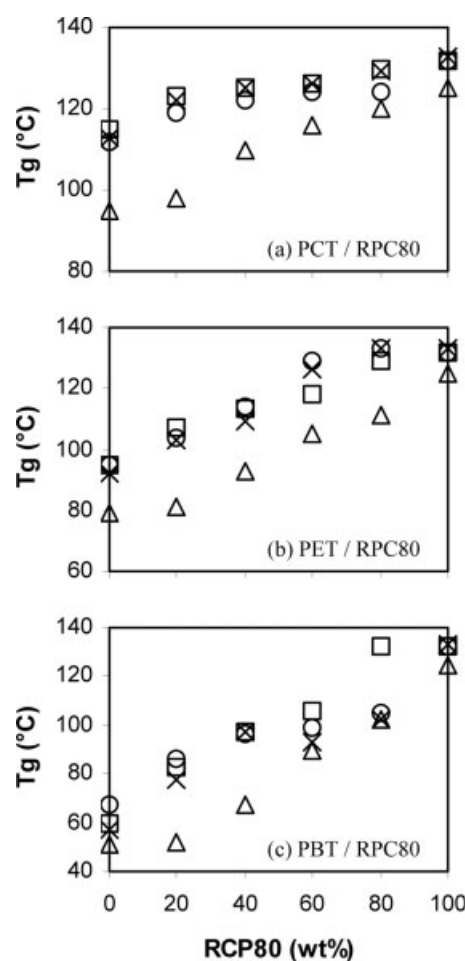


Figure 9 Glass transition temperature of RPC80 blends with PCT (a), PET (b), or PBT (c) before and after annealing by using DMA. RPC80 (100%) sample was annealed at 140°C for 1 day because 165 and 190°C are higher than T_g of the material. (□: annealed at 190°C for 1 h, ○: annealed at 165°C for 1 day, ×: annealed at 140°C for 1 day, and △: not annealed).

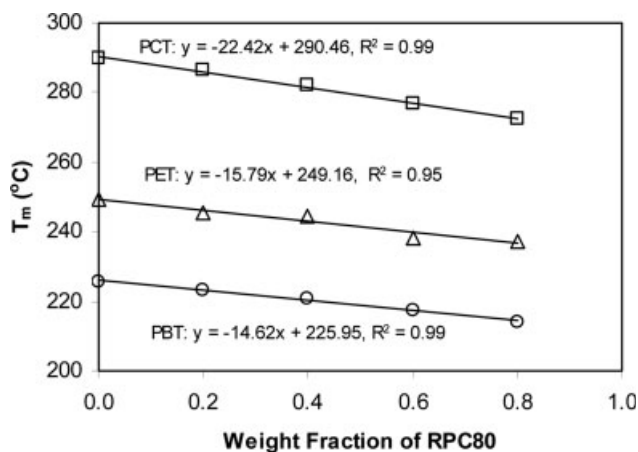


Figure 10 Melting-point depression of polyesters (\square : PCT, \triangle : PET, and \circ : PBT) in blends with RPC80. The melting points were measured on extruded pellets by DSC with a heating rate $20^\circ\text{C}/\text{min}$. The melting points are average of four measurements where melting point was measured from first and second heating for two samples. Standard deviation of the melting points was 1.5°C on an average.

In contrast, the blend of RPC80 and PCCD showed two separated T_g 's even after the blends were annealed at 140 , 165 , or 190°C for 1 day.

Melting-point depression

DSC curves for RPC80 blend with PET, PBT, PCT, or PCCD are shown in Figures 4 and 7. The melting point of the polyesters in the blends was used to estimate the degree of miscibility of the blends.³⁴ Further analysis on the melting-point depression was limited to miscible blends of PET, PBT, and PCT. The melting points of PET, PBT, and PCT are depressed at higher amounts of RPC80 in the blend, indicating all three polyesters are miscible with RPC80. Figure 10 summarizes the empirical correlation between the melting point of the polyesters and the weight fraction of RPC80. In the empirical correlation, the slope of the linear regression indicated that RPC80 had a larger effect on the melting point of PCT than PET or PBT.

To investigate the effect of the molding process, parts (63.5 mm long, 12.7 mm wide, and 3.2 mm thick) were molded with the extruded pellets. Figure 11 compares the melting points of parts and pellets. Within the experimental error, the melting points of extruded pellets have not changed after molding, indicating that the molding process, second heat history after extrusion, did not cause substantial change in the phase behavior of the blends.

As the melting point of water decreases with higher amounts of soluble salts, the melting point of a semicrystalline polymer decreases in the miscible blends. The degree of miscibility can be quantified by the degree of the depression in the melting point

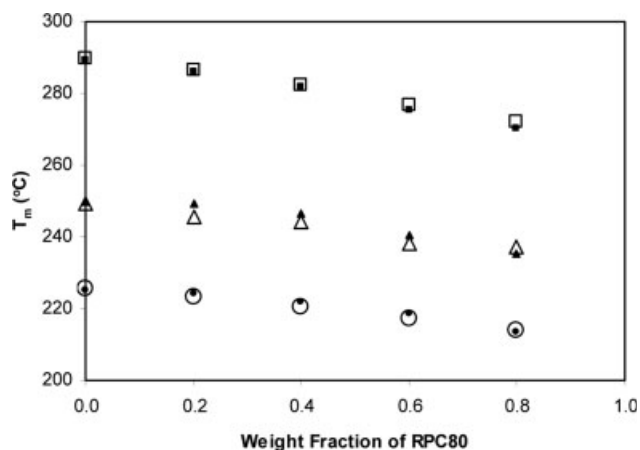


Figure 11 Processing effect on the melting-point depression of polyesters in blends with RPC80. Open symbols represent extruded pellets and closed symbols represent molded parts (rectangles: PCT, triangles: PET, and circles: PBT). The melting points were measured on extruded pellets by DSC with a heating rate $20^\circ\text{C}/\text{min}$.

of the semicrystalline polymer. The Flory interaction parameter χ_{12} for the blend of amorphous Polymer 1 and semicrystalline Polymer 2 can be calculated by using Nishi–Wang equation.³⁴

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_1\chi_{12}\phi_1^2}{\Delta H_f V_2} \quad (2)$$

where T_m and T_m^0 are the thermodynamic melting points of semicrystalline Polymer 2 in the blends and in the homopolymer, respectively. R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), ΔH_f is the heat of fusion per mole of crystalline repeat units, V_1 and

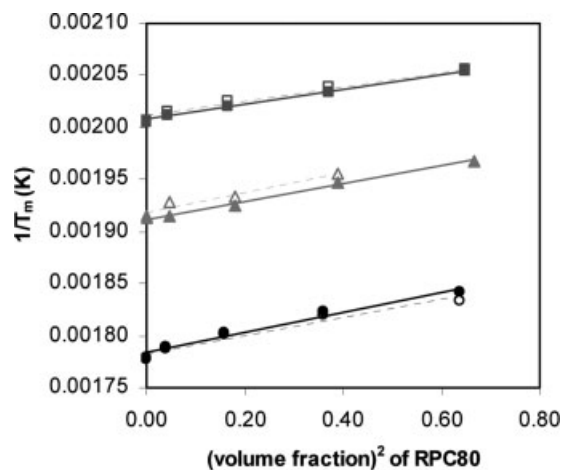


Figure 12 Analysis of melting-point depression of RPC80 blend with PCT, PET, or PBT by using Nishi–Wang equation. Open symbols are extruded pellets and closed symbols are molded samples after extrusion (\square : PCT, \triangle : PET, \circ : PBT). The trend lines were based on the Nishi–Wang equation.

TABLE IV
Parameters Used in Nishi–Wang Equation

	d_a (g/cm ³)	d_c (g/cm ³)	ΔH_f° (J/mol)	M (g/mol monomer)	ΔH_ϕ° (J/g)	V_c (cm ³)	V_a (cm ³)
PET	1.332	1.462	25000	192	130	131.3	144.2
PBT	1.244	1.370	33000	220	150	160.6	176.9
PCT	1.191	1.316	54400	274	199	208.2	230
RPC80	1.322			243			183.7

Density and heat of fusion were calculated by van Krevelen methods and verified with experimental values in case experimental values are available. Data in the table are calculated values. d_a , density of amorphous phase; d_c , density of 100% crystalline phase; ΔH_f° , heat of fusion of 100% crystalline polymer, based on data in van Krevelen;³⁸ ΔH_ϕ° is the same as ΔH_f° in different unit (J/g); M (g/mol monomer), molecular weight of a repeat unit; V_c (cm³), molar volume of a repeat unit in crystalline phase; V_a (cm³), molar volume of a repeat unit in amorphous phase.

V_2 are the molar volumes of the amorphous and crystalline polymer repeat units, and ϕ_1 is the volume fraction of amorphous Polymer 1. The entropy contribution was neglected due to the high molecular weight of the polymers in the study. Note that the melting points in this study were not thermodynamic melting points. Hence, the analytical results from eq. (2) give only approximated values.

The interaction parameters in the three polyester blends were obtained from the slope of T_m^{-1} versus ϕ_1^2 plots in Figure 12. Tables IV and V summarize results of the analysis on the three blend systems and parameters used for Nishi–Wang equation. It is worthy to note that the difference of the Flory interaction parameter between pellets and parts is not substantial, considering the standard deviation of the interaction parameters in the table. The calculated values of interaction parameters indicate that PCT has a stronger attraction to RPC80 than PBT or PET. The conclusion based on the Nishi–Wang equation agreed with the empirical correlation in Figure 10.

DISCUSSION

Quantitative analysis on the degree of miscibility of the blends can be conducted based on the Flory equation.³⁵ The interaction parameter χ_{12} , defined by Flory is proportional to the enthalpy of mixing of the polymer mixture. The product of χ_{12} and the thermal energy, i.e., kT , where k and T are the Boltzman constant and temperature, respectively, is the difference in energy of a repeating unit 1 immersed in the pure Polymer 2 compared with the repeat unit 1 surrounded by molecules of its own kind, i.e., in the pure Polymer 1. At a given volume, the enthalpy change upon mixing of Polymers 1 and 2 can be expressed by

$$\Delta H_M = kT\chi_{12}n_1\phi_2 \quad (3)$$

where n_1 and ϕ_2 are the number of the repeat unit 1 and the volume fraction of Polymer 2 in the mixture, respectively. When two high molecular weight polymers form a mixture, due to a substantial small entropy of mixing, the enthalpy of mixing is the critical

factor to determine the miscibility of the polymers. A negative χ_{12} value indicates that the polymer blend should be miscible. A negative χ_{12} value is obtained due to attractive interactions such as the dipole–dipole interaction, polar interaction, and/or hydrogen bonding between repeating units of Polymers 1 and 2.

The value of χ_{12} may be calculated from the solubility parameters as shown in eq. (4),

$$\chi_{12} = \frac{V_x(\delta_1 - \delta_2)^2}{RT} \quad (4)$$

where V_x , δ_1 , and δ_2 are the molar volume of the repeat unit, solubility parameters of Polymers 1 and 2, respectively. The smaller difference in the solubility parameters predicts higher possibility of miscibility of the two polymers. However, eq. (4) cannot predict attractive interactions with a negative χ_{12} .

Empirical calculations, based on molar group contributions, have been used to estimate solubility parameters. Small,³⁶ Hoy,³⁷ and van Krevelen³⁸ use the relationship:

$$\delta = \frac{\sum F_i}{V} \quad (5)$$

where F_i and V are the molar attraction constant and molar volume of a repeat unit, respectively.

TABLE V
The Interaction Parameters of Polyesters with RPC80 from Nishi–Wang equation

Blends	Sample type	R^2	χ_1	$\sigma(\chi_1)$
RPC80/PET	Pellets	0.935	−0.40	0.07
	Molded parts	0.996	−0.36	0.01
RPC80/PBT	Pellets	0.963	−0.32	0.04
	Molded parts	0.999	−0.33	0.01
RPC80/PCT	Pellets	0.953	−0.49	0.06
	Molded parts	0.967	−0.54	0.06

R^2 , R -square of linear regression based on Nishi–Wang equation; χ_1 , Flory interaction parameter; $\sigma(\chi_1)$, standard deviation of the interaction parameter based on standard deviation of the slope in Nishi–Wang equation.

TABLE VI
Solubility Parameters and Physical Properties Used to Calculate the Solubility Parameters

	PC	RPC80	PET	PBT	PCT	PCCD
Density ^a (g/cm ³)	1.20	1.32	1.33	1.24	1.19	1.12
M_w (g/mol)	254	243	192	220	274	280
V (cm ³ /mol)	211	184	144	177	230	250
δ by Small's method (cal/cm ³) ^{0.5}	9.7	10.7	10.7	10.3	9.3	8.3
δ by Hoy's method (cal/cm ³) ^{0.5}	10.4	11.4	11.3	10.7	10.1	9.3
δ by Krevelen's method (cal/cm ³) ^{0.5}	10.1	11.0	10.1	9.8	9.3	8.6
δ by Coleman's method (cal/cm ³) ^{0.5}	10.4	11.7	11.5	10.8	10.4	9.5

M_w , molecular weight of a repeat unit; V , molar volume of a repeat unit in amorphous phase; δ , solubility parameter.
^a Calculated density of amorphous phase (cm³/g) by van Krevelen's method.³⁸

Coleman et al.³⁹ suggested practical guides for predicting and designing miscible polymer mixtures. They categorized polymer blends based on the interactions between two polymers. The miscibility of the polymer blends was determined by two factors: (1) the difference in solubility parameters ($\delta_1 - \delta_2$) and (2) $(\delta_1 - \delta_2)_{\text{critical}}$, which depends on the interaction between the polymers. A system with a stronger interaction has a higher $(\delta_1 - \delta_2)_{\text{critical}}$. Polymer pairs with $(\delta_1 - \delta_2) < (\delta_1 - \delta_2)_{\text{critical}}$ should be miscible by the prediction.

Table VI summarizes the solubility parameters of RPC80, PET, PBT, PCT, and PCCD. Calculated values, based on all four methods, predict that the solubility parameters are in the following order:

$$\text{RPC80} > \text{PET} > \text{PBT} > \text{PCT} > \text{PCCD}$$

The calculated solubility parameters are in agreement with the experimental data on the blends of RPC80 and the polyesters except the blend of RPC80 and PCT. The calculated values of solubility parameters failed to predict good miscibility of RPC80 and PCT. At this moment, it is not fully understood why the four methods do not predict the best miscibility of RPC80 and PCT. However, as suggested by Coleman et al.,³⁹ the specific interaction, i.e., $(\delta_1 - \delta_2)_{\text{critical}}$, between RPC80 and PCT might be considerably larger than that between RPC80 and PET or PBT. The interaction between RPC80 and PCT might be stronger than that of other blends probably due to the similarity in the size of PCT unit and RPC80 unit.

CONCLUSIONS

We report for the first time the phase behavior of RPC with the engineering polyesters. RPC80 was found to form miscible blends with PET, PBT, and PCT. However, it was partially miscible with PCCD.

The melting-point depression and glass transition temperature were used to study the miscibility at various temperatures qualitatively and quantitatively. The observation of a single glass transition temperature indicated that RPC80 was miscible with

PET, PBT, and PCT. However, the existence of two glass transitions in the blends of RPC80 and PCCD suggested they were partially miscible. Further annealing studies indicate that the miscibility of RPC80 with PET, PBT, PCT, or PCCD did not change in the annealing temperature range from 140 to 190°C, as was found by DMA measurements. Melting-point depression by DSC indicated that RPC80 had maximum miscibility with PCT. The interaction parameters between RPC80 and PET, PBT, and PCT were -0.36 , -0.33 , and -0.54 , respectively, by using Nishi-Wang equation.

Solubility parameters of the polyesters were calculated by Small,³⁶ Hoy,³⁷ and van Krevelen³⁸, and Coleman's³⁹ methods. The calculated solubility parameters were in agreement with the experimental data on the blends of RPC80 and the polyesters except the blend of RPC80 and PCT. As suggested by Coleman et al.,³⁹ the specific interaction, i.e., $(\delta_1 - \delta_2)_{\text{critical}}$, between RPC80 and PCT might be considerably larger than that between RPC80 and PET or PBT. However, it calls for a further study to quantify the specific interactions in the current blend systems.

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