Polymer 51 (2010) 2199–2206

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

The phase behavior and the Flory–Huggins interaction parameter of blends containing amorphous poly(resorcinol phthalate–*block*-carbonate), poly-(bisphenol-A carbonate) and poly(ethylene terephthalate)

Sung Dug Kim [a,*], Shreyas Chakravarti [a], Jun Tian [b], Philip Bell [a]

[a] SABIC Innovative Plastics, Global Crystalline Polymer Technology, One Lexan Lane, Mount Vernon, IN 47620, USA
[b] SABIC Innovative Plastics, Analytical Technology, One Lexan Lane, Mount Vernon, IN 47620, USA

ARTICLE INFO

Article history:
Received 5 January 2010
Received in revised form
2 March 2010
Accepted 6 March 2010
Available online 18 March 2010

Keywords:
Polyesters
Copolymer of resorcinol and carbonate
Flory–Huggins interaction parameter

ABSTRACT

The phase behavior of the blends of poly(ethylene terephthalate) (PET) and poly(Resorcinol Phthalate-*block*-Carbonate) (RPC) and the blends of PET and poly(Bisphenol-A Carbonate) (PC) was investigated by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). Blends of high molecular weight PET and RPC copolymer with 20 mol% resorcinol phthalate (RPC20) showed two glass transition temperatures in DMA and DSC but the cold crystallization rate of PET phase was substantially lowered as compared to neat PET, indicating partial miscibility at all compositions. The RPC20 with $M_w = 31{,}500$ g/mol formed miscible blends with PET when PET has weight-average molecular weight <9500 g/mol. The Flory–Huggins interaction parameter between PET and RPC20 was calculated to be 0.029 ± 0.003 by using the Flory–Huggins equation at critical composition and molecular weight. PC with $M_w = 30{,}000$ g/mol formed miscible blends with PET only when PET had molecular weight <2800 g/mol, indicating PC/PET blends were much less miscible than RPC20/PET blends. Group contribution methods agreed well with the experimental results obtained both in the present study and a previous study [1], predicting that the addition of a resorcinol phthalate block to a PC backbone should increase the miscibility of PC and PET.

1. Introduction

PET is one of the most widely used semi-crystalline polyesters in industry. Good chemical resistance and tensile strength make PET a useful polymer in applications including films, fibers, or bottles. Bisphenol- A Polycarbonate (PC) is another important engineering plastic due to its high impact resistance and optical clarity. Blends of PET and PC are commercially successful because of the balance of properties imparted by semi-crystalline PET and impact resistant PC. One of the keys to making useful blends of PET and PC is to control their morphology based on a good understanding of their miscibilities. Kong and Hay [2] investigated transesterification of PET and PC to conclude that PC and PET with a number-average molecular weight of ~20 kg/mol were completely immiscible in the absence of a transesterification catalyst. Paul et al. reported that the blends were miscible with high PET content above 60–70% and immiscible in other compositions [3,4]. Other researchers found that the blends were immiscible at all compositions [5,6]. Recently, Kong and Hay [2] provided a brief summary on PET and PC blends, and they attributed the discrepancy in the literature to sample preparation methods, transesterification, and analytical methods.

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 and outdoor environments. In addition, UV additives tend to degrade over time and do not protect the polymer matrix during the complete course of its expected lifetime. Some engineering plastics inherently have robust UV stability due to their chemical structure. To overcome the aforementioned migration issue, UV resistant engineering plastics can be used with or without blending with other polymers. The effectiveness of the UV resistant polymer in the blends can be dramatically different for a miscible blend vs. an immiscible blend. For immiscible or partially miscible blends, the blend morphology can play an important role. Therefore, it is critical to understand the miscibility of UV resistant polymers with other polymers. RPC is relatively less known to the polymer industry. Based on the limited literature [7,8] available,

---

[*] Corresponding author. Tel.: + 1 812 831 4683.
E-mail address: sungdugkim@gmail.com (S.D. Kim).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.03.018

excellent physical properties, chemical resistance and UV resistance properties have been reported. It has also been reported that RPC is miscible with polyetherimide [9], and has formed useful blends with polycarbonate [10].

In the present study, we investigated the miscibility of PET and PC copolymers containing resorcinol comonomer. Poly(resorcinol phthalate-*block*-carbonate) with 20 mol% resorcinol (RPC20) was made to improve the UV resistance of polycarbonate and its blends. The present study explores whether resorcinol phthalate in the copolymer substantially changes the miscibility of PET and PC and furthermore changes overall properties of the blend.

In a previous study, S. D. Kim et al. [1] reported that RPC containing 80 mol% resorcinol phthalate formed miscible blends with PET. The Flory–Huggins interaction parameter was quantified to be −0.33 by using the Nishi–Wang equation. In the present study, we focused on RPC with a relatively low resorcinol content of 20 mol%.

The phase behavior was studied by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Transmission electron microscopy (TEM) provided additional information on the phase behavior at a microscopic level when the blends showed rather broad peaks in DMA. The samples in the present study were prepared by extrusion or extrusion followed by molding to simulate blend properties in practical applications. Solution blending was also performed for low molecular weight PET samples.

2. Experimental section

2.1. Materials

Poly(resorcinol phthalate-*block*-carbonate) (Fig. 1) was obtained from Sabic Innovative Plastics Co.(formerly GE Plastics) and its weight-average molecular weight in Table 1 was measured against polycarbonate standards by gel permeation chromatography (GPC). The synthetic scheme has been published elsewhere [7]. RPC was a multi- block copolymer with BPA based carbonate repeating units and resorcinol phthalate repeating units. In the resorcinol phthalate block, a 1/1 mol ratio of isophthalic and terephthalic acids was used. RPC20 corresponds to an RPC copolymer with 20 mol% resorcinol phthalate repeating units.

Commercial PET samples were obtained from DuPont Chemical Co. Low molecular weight PET samples were synthesized from dimethyl terephthalate (Eastman Chemical, 99+%) and ethylene glycol (Fisher Scientific, 99.5+%) by melt phase polymerization. The ester interchange reaction was carried out from 170 to 230 °C in the presence of 200 ppm of manganese acetate tetrahydrate (Acros, 99+%). The polymerization was carried out from 250 to 280 °C under vacuum in the presence of 200 ppm of antimony oxide (Aldrich, 99+%) as the polymerization catalyst. Samples were taken at different points during the polymerization reaction by breaking vacuum, allowing the synthesis of a wide range of average molecular weights. The polymer pellets were extruded with stabilizers of Sandostab P-EPQ and mono zinc phosphate [11,12] 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 a screw speed between 150 and 300 rpm. The extruder can be operated at a maximum rate of 30 kg/h. Different ingredients can be conveniently added to the extruder by use of 8 independent feeders. 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 approximately 250–270 °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 (DMA) 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.

Table 1
Molecular weight of materials by gel permeation chromatography (GPC).

Polymer	M_w (g/mol)	M_n(g/mol)	T_g,DSC (°C)
PET-A[a]	88,000	47,000	76
RPC20[b]	31,500	12,000	140
PC[b]	30,000	12,000	147

[a] Against polystyrene standards.
[b] Against polycarbonate standards.

Solution blending was performed for blends containing low molecular weight PET. The blends of PET at various weight ratios were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The solution typically had less than 5% by weight of polymers to form transparent solutions. If the solution became turbid, more HFIP was added until the solution became optically transparent. The solution was then precipitated into an excess amount of methanol. The mixture of methanol, HFIP, and precipitated polymers was dried under air. The precipitated powder was dried at room temperature overnight and then dried at 120 °C for 3–4 h before compression. Films were obtained by compression molding between Teflon sheets with 300 μm thick spacers at 270 °C ± 10 °C for 30 s, followed by quenching between cold metal plates.

2.2. Measurements

Differential Scanning Calorimetry (DSC): Thermal transitions, including the glass transition, melt, and crystallization temperatures and the enthalpies of melting and crystallization of the blends, were measured on a differential scanning calorimeter (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 [6,13–18] 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. In order to avoid confounding of results by transesterification for this study, it was ensured that the experimental conditions were optimized to minimize transesterification [1].

Dynamic Mechanical Analysis (DMA): Dynamic mechanical properties of the blends were evaluated with a TA instrument TA 2980 or TA Q800. The extruded pellet blends were heat pressed into

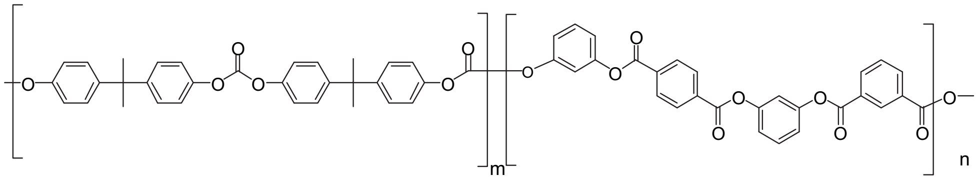

Fig. 1. Poly(resorcinol phthalate-*block*-carbonate) (RPC).

a thin film, and a strip was cut out to fit into a film extension fixture. All the samples were annealed at 150 °C for 4 h before loading onto the DMA for testing. Small amplitude tensile deformation was used with a frequency of 1 Hz. Temperature was increased from room temperature to 200 °C at a ramp rate of 3 °C/min.

Nuclear Magnetic Resonance (NMR) spectroscopy: The molecular weight of the PET samples was determined by end group analysis with an Oxford NMR AS400 instrument. The end-group determination was done according to the method developed by Donovan and Moad [19] in combination with measurements of PET dissolved in tetrachloroethane-1,2-d_2 (TCE). The acid and hydroxyl end-groups were reacted with trichloroacetyl isocyanate (Sigma–Aldrich, 97+%) in TCE to form derivatives that were easily quantifiable in the NMR spectra. Example spectra are shown in Fig. 2. From measurements of the PET derivitives, the concentration of carboxylic acid ($\delta \sim 10.26$ ppm) and alcohol end groups ($\delta \sim 8.53$ ppm) were directly determined. The concentration of alcohol end groups determined by this method was used to verify the alcohol end groups determined by measurement of the polymer dissolved in TCE ($\delta \sim 4.0$ ppm). Because our polymers were made using dimethyl terephthalate as a monomer, the PET also contained methoxy end groups. These were determined directly from ^{1}H NMR measurements of PET dissolved in TCE ($\delta \sim 3.95$ ppm). The number-average molecular weight was directly calculated from the concentration of end-groups.

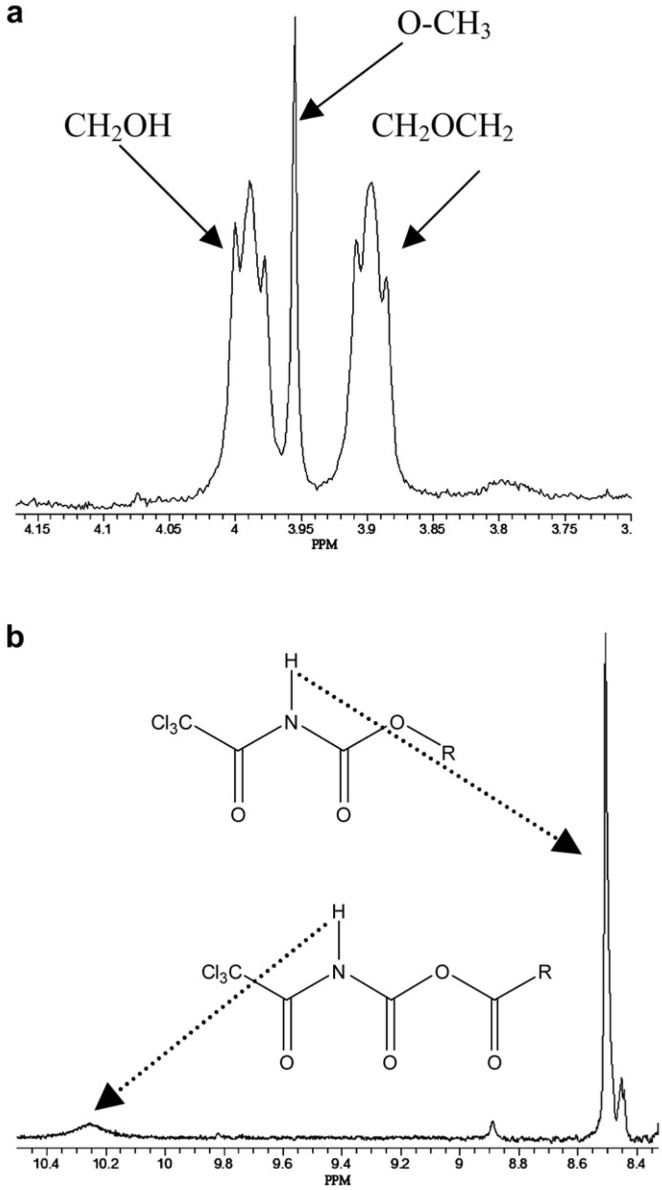

Fig. 2. ^{1}H NMR spectra of PET in TCE showing peaks for (a) alcohol and methoxy end groups (b) derivitized carboxylic acid and alcohol end groups.

The molecular weight of PET was obtained by both GPC and NMR methods. The theoretical calculation in the present study requires the absolute weight-average molecular weight (M_w). While GPC provides information on both the number-average molecular weight (M_n) and the weight-average molecular weight (M_w), the molecular weight of PET from GPC was not absolute due to the use of polystyrene as standard samples. In contrast, NMR offers an absolute M_n, but it does not provide M_w. Fig. 3 correlates M_n by NMR and M_n by GPC on broad range of molecular weight. The correlation in Fig. 3 was used to convert M_n and M_w from GPC to absolute M_n and M_w. The molecular weight of PET in the present study is absolute M_n and M_w unless specified otherwise. Table 2 summarizes absolute M_n and M_w of PET used in the present study.

3. Results

The miscibility of the blend of RPC and polyesters was investigated by DMA, DSC, and TEM.

3.1. High molecular weight PET blends

Fig. 4 shows the glass transition temperature of the PC/PET blends as determined from DMA data of the molded bars. The glass transition temperatures at about 80–90 °C and 130–150 °C are attributed to the PET phase and the PC phase, respectively. The DMA data displays two glass transitions for all the blends, indicating PC and PET form immiscible blends. The fact that PET and PC were immiscible in the present study agrees with most of the studies on PET and PC in the absence of a transesterification catalyst [2]. In the present study, the blends were stabilized by using a quencher (i.e. mono zinc phosphate to deactivate catalyst) to inhibit transesterification [12].

Fig. 4 also shows the DMA data of the molded bars from the blends of RPC20 and PET. The DMA data displays two glass transitions except the blends containing less than 25% PET and more than 85% PET. The glass transition temperatures at around 80–90 °C and 130–150 °C are attributed to the PET phase and the RPC20 phase, respectively. The blends containing less than 25% PET and more than 85% PET did not show T_g of PET phase or RPC20 phase probably

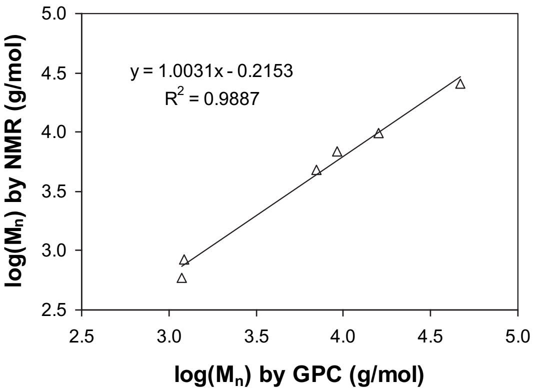

Fig. 3. Correlation of number-average molecular weight of PET samples measured by GPC and NMR.

Table 2
Absolute molecular weight and glass transition temperature of PET samples used in the present study.

	M_n(g/mol)	M_w (g/mol)	T_g, DSC (°C)
PET_1.2k	737	1262	17
PET_2.8k	1104	2757	25.6
PET_4.1k	2017	4128	51.5
PET_9.5k	4374	9521	69.6
PET_13.2k	5779	13199	71.9
PET_14.4k	5905	14383	72.7
PET_14.5k	6010	14495	73.5
PET_14.9k	5922	14879	73.9
PET_29.0k	9724	28058	75.3
PET_29.5k	9755	29511	75.7
PET_34.5k	10004	34563	76.1

Commercial high molecular PET (nominal intrinsic viscosity = 0.8 g/dl from Dupont company) has $M_n = 29{,}600$ g/mol, $M_w = 55{,}500$, and $T_g = 76.9$ °C.

due to peak broadening in DMA loss modulus in these compositions. Complementary information from TEM in Fig. 5 illustrates phase separation in all compositions including blends containing 10% PET and 90% PET, indicating that RPC20 is not miscible with high molecular weight PET. RPC20 is expected to form spherical domains at low concentrations, co-continuous cylindrical domains at medium concentrations, and matrix surrounding spherical domains at high concentrations

Fig. 6 compares DSC traces of PET and its blends upon heating from a quenched status. Evidently, crystallization occurs for all four samples. Generally, the crystallization temperature upon heating from a quenched status is lower than the one seen upon cooling from the melt, therefore this crystallization is usually referred to as cold crystallization [20]. Neat PET had a cold crystallization peak at ~125 °C. PET in PET/PC blends displayed cold crystallization at the same temperature of ~125 °C, indicating that PET domains were phase separated from PC domains and PET crystallization behavior in PET/PC blend was not much different from that of neat PET. PET in PET/RPC20 blends displayed cold crystallization at 10 °C higher than neat PET, indicating that crystallization of PET was slowed down in the presence of RPC20. Slower crystallization of PET in PET/RPC20 blends is attributed to *partial* miscibility of the blends. In miscible or partially miscible blends, PET molecules are required to diffuse through RPC20 molecules before forming pure PET crystalline domains. Consequently, the crystallization rate of PET in miscible/partially miscible blends should be reduced in more miscible blends and higher concentration of its counter part. The last example of PET/RPC80 was found to be fully miscible in our previous study [1]. As expected, cold crystallization of PET in PET/RPC80 was substantially lowered to 170 °C. We have defined high molecular weight PET/RPC20 blends as partially miscible blends based on the cold crystallization behaviors.

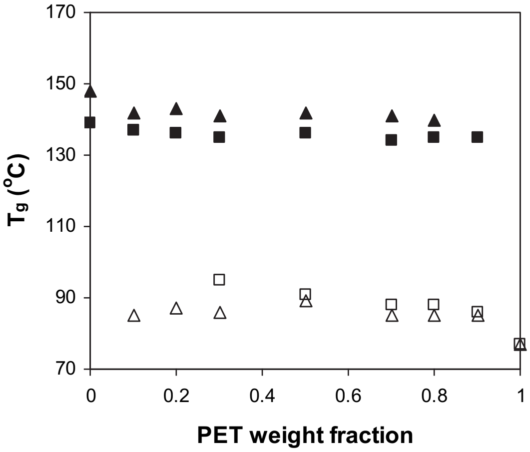

Fig. 4. Glass transition temperature of PC/PET blends (triangles) and RPC20/PET blends (rectangles) by DMA loss modulus.

3.2. *Low molecular weight PET blends*

A typical polymer blend may be immiscible because the entropy gain upon mixing is too small to overcome unfavorable interactions between polymers. The miscibility can be improved by reducing the molecular weight of one or both of the polymers or by incorporating comonomers into one or both of the polymers. When the molecular weight is substantially reduced or the comonomer concentration is high enough, the transition from an immiscible blend to a miscible blend can be observed by readily available instrumentation such as DSC.

In the present study, low molecular weight PET samples and RPC20 or PC were prepared by solution mixing. Blends were prepared using a solution precipitation procedure similar to Kimura et al. [21].. Solution precipitation was used because a casting method may cause undesired phase separation during drying process. The films were quenched from the melt to room temperature to inhibit crystallization. The quenching process was efficient enough that neat PET films were optically transparent. Because low molecular weight PET blends do not have enough mechanical strength for DMA measurements, the blend films were tested only by DSC.

A typical DSC curve is shown in Fig. 6. As a film was heated up, the glass transition temperature of the PET phase was observed at around 80 °C followed by a crystallization peak at around 130 °C. The presence of a crystallization peak indicates that the quenching protocol sufficiently suppressed crystallization of PET. Since the crystallization peak appears around the glass transition temperature of PC and RPC20 and the magnitude of the crystallization peak is much larger than the glass transition of PC and RPC20, the glass transition temperature around 130–150 °C was not observed in most samples. Hence, discussion below is focused on the glass transition of PET around 80 °C.

Fig. 7 summarizes T_g of neat PET and T_g of PET in the blends with PC. T_g of neat PET decreased as molecular weight decreased below a certain molecular weight. The reduction in glass transition temperatures with lower molecular weight can be explained by the well known Fox–Flory equation [22,23].

$$T_g = T_{g\infty} - K_g/M_n \qquad (1)$$

where $T_{g\infty}$ (in K), M_n(in g/mol), and K_g (in Kg/mol))are the glass transition temperature for an infinite molecular weight, number-average molecular weight, and a characteristic parameter of the polymer, respectively. The linear regression with equation (1) and the data in Table 2 resulted in $T_{g\infty} = 353.5$ K (80.36 °C) and $K_g = 47784$ Kg/mol with a regression $R^2 = 0.95$. It is interesting to note that the glass transition temperature of PET has been used as an example to resolve contradictory proposals. Hintermeyer et al. [24] proposed that the molecular weight M_w at which the T_g reaches a plateau corresponds to the molecular weight between entanglements, M_e. In contrast, Agapov and Sokolov [25] more recently proposed that there is no relationship between M_e and saturation of the molecular weight dependence of T_g. The data in the present report shows that T_g of PET did not reach to $T_{g\infty}$ at the entanglement molecular weight ($M_e \approx 1170$ g/mol [26]), supporting Agapov and Sokolov's proposal.

We also fit the T_g data to M_w by using equation (1) and replacing M_n with M_w. A linear regression resulted in $T_g = 77.7–78885/M_w$

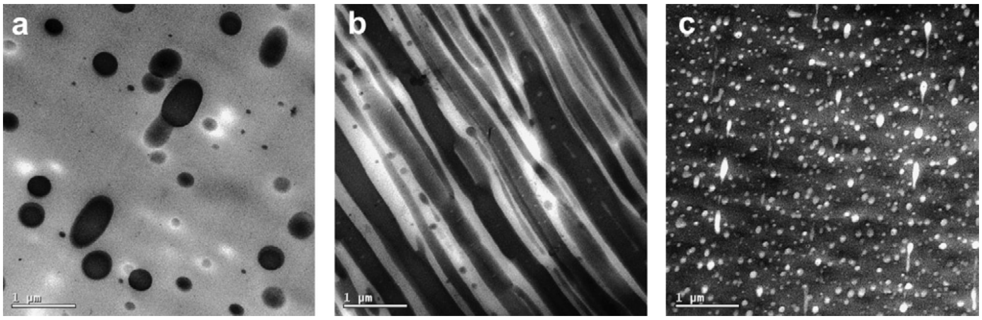

Fig. 5. TEM of RPC20 and PET-A blends: (a)10 wt% RPC20, (b)50% RPC20, and (c) 90% RPC20. The scale bars in the TEM pictures are 1 μm RPC20 is shown as dark phase due to RuO_4 staining.

with $R^2 = 0.97$. This equation is used in Figs. 7 and 8 where weight-average molecular weight is a critical variable to compare the experimental data points. The dotted line in Fig. 7 is the calculated T_g of miscible blends of PC and PET where neat PC has a T_g of 147 °C and neat PET has various T_g as a function of molecular weight.

The T_g of the PET phase in the blends of PC and PET is shown in Fig. 7. As described above, the T_g of the PC phase is not reported due to the overlap between the T_g of PC and the crystallization peak of PET. If a blend with a higher T_g resin is miscible, the T_g of the blend is expected to have 1 T_g between the glass transition temperatures of the neat polymers and to be similar to the calculated T_g by the Fox equation [27] or any equivalent equations. When the weight-average molecular weight of PET is higher than ~5000 g/mol, the T_g of the PET phase in the blends is almost the same as the T_g of neat PET, indicating that PET and PC are immiscible. However, the blend of PC and the lowest molecular PET (M_n = 1400 g/mol) has a T_g much higher than the T_g of neat PET and similar to the T_g calculated by the Fox equation, indicating that the blend is miscible. Based on the data in Fig. 7, the transition from miscible to immiscible blends of PC and PET occurred when PET has a weight-average molecular weight between 2760 and 4130 g/mol.

Fig. 8 summarizes T_g of PET in the blends of RPC20 and PET as determined by DSC. The dotted line in Fig. 8 represents the calculated T_g of miscible blends of RPC20 and PET where neat RPC20 has a T_g of 140 °C and neat PET has various T_g as a function of molecular weight. When the weight-average molecular weight of PET is higher than ~13,200 g/mol, the T_g of the PET-rich phase in the blends is slightly higher (~5 °C) than the T_g of neat PET but much lower (20–25 °C) than the T_g of miscible blends calculated from the Fox equation, indicating that PET and RPC20 are immiscible. The slightly higher T_g of the blends than neat PET is not fully understood yet. However, when the weight-average molecular weight of PET is lower than ~9500 g/mol, the T_g of the PET phase in the blends is much higher than the T_g of neat PET and similar to the T_g of miscible blends calculated from the Fox equation, indicating that PET and RPC20 are miscible. Based on the data in Fig. 8, the transition between miscible to immiscible blends of PC and PET occurred when PET has a weight-average molecular weight between 9520 and 13,200 g/mol.

The transition from immiscible blend to miscible blend can be utilized to calculate the Flory–Huggin's interaction parameter [28]. The Gibbs free energy of mixing per volume is given by [29]:

$$\frac{\Delta G_m}{RT} = \frac{\varphi_1}{N_1 v_1}\ln\varphi_1 + \frac{\varphi_2}{N_2 v_2}\ln\varphi_2 + \frac{\chi_{12}}{v}\varphi_1\varphi_2 \tag{2}$$

where ϕ_1 and ϕ_2 are the volume fractions and N_1 and N_2 are degrees of polymerization for polymer 1 and 2 respectively, χ_{12} is the Flory interaction parameter, v_1 and v_2 are the average molar volumes of repeating units of polymer 1 and 2, v is the reference volume (taken equal to the smallest of v_1 or v_2). In the present study, polymer 1 is PET and polymer 2 is PC or RPC20.

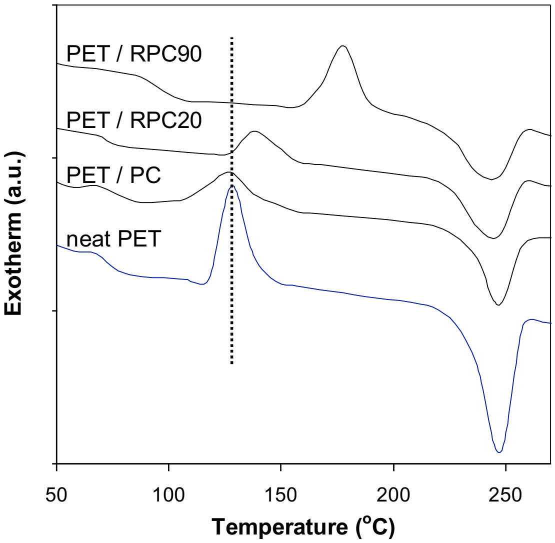

Fig. 6. DSC traces of neat PET and PET blends. The blend samples have 60 wt% of PET and 40% of PC, RPC20, or RPC80. Samples were quenched before DSC experiments and are expected to have no or suppressed crystallinity. Quenched samples were heated at 20 °C/min for DSC scan. The vertical dotted line is present to guide the eye. DSC traces were shifted to *y*-axis.

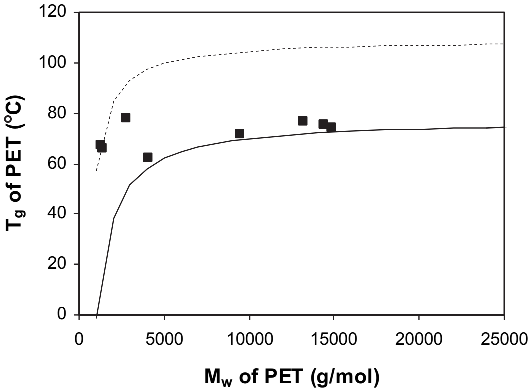

Fig. 7. Glass transition temperature, T_g, of neat PET (circles), T_g of PET in the blends of 50 wt%/50 wt% PET/PC (rectangles). The solid line represents the calculated T_g of neat PET based on DSC data in Table 2 (T_g (°C) = $-78885/M_w + 77.7$, with a linear regression $R^2 = 0.966$) and dotted line represents T_g of PET from the Fox equation for 50 wt%/50 wt% PET/PC.

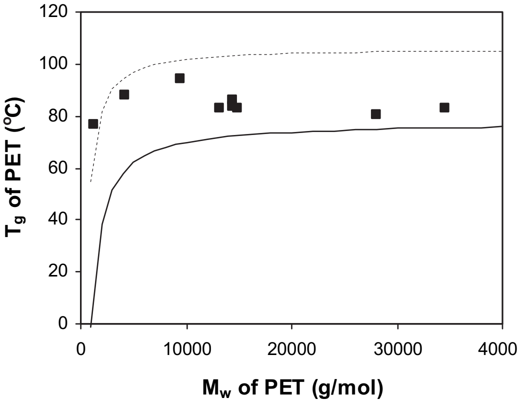

Fig. 8. Glass transition temperature, T_g, of neat PET (circles), T_g of PET in the blends of 50 wt%/50 wt% PET/RPC20 (rectangles). The solid line represents the T_g of neat PET and dotted line represents T_g of PET from the Fox equation for 50 wt%/50 wt% PET/RPC20.

For a stable one-phase binary system, the following two conditions should be satisfied with composition ϕ at fixed temperature T and pressure P [30]

$$\Delta G_m < 0, \quad \left(\frac{\partial^2 \Delta G_m}{\partial^2 \varphi}\right)_{P,T} > 0 \tag{3}$$

By combining equations (2) and (3), it is concluded that the miscibility can only be achieved when $\chi < \chi_{cr}$ where the χ parameter at the critical point χ_{cr} is defined by:

$$\chi_{cr} = \frac{1}{2}\left[\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2(v_1/v_2)}}\right]^2 \tag{4}$$

where the degree of polymerization can be obtained by using the weight-average molecular weight in the present study with a broad molecular weight distribution [31]. The Flory–Huggins interaction parameter is found to be $\chi < \chi_{cr}$ for miscible blends or $\chi > \chi_{cr}$ for immiscible blends. In the present study, experimental data with various weight-average molecular weights of PET was used to define the range of interaction parameter.

In Table 3, the Flory–Huggins interaction parameter, χ, was calculated for PC/PET blends and RPC20/PET blends. PC/PET blends have a substantially larger χ value than RPC20/PET blends. It is worth noting that the PC/PET blend became miscible at only a very low molecular weight of PET, and hence the interaction parameter might be less accurate than that of RPC20/PET blends due to end-group effects. In contrast, the χ parameter of 0.031 for RPC20/PET blends was obtained from relatively high molecular weight PET of ~10,000 g/mol, though still low compared to typical PET, and hence the χ value should be less affected by end-groups. Nonetheless, the experimental data and calculated χ parameter indicates that introducing 20% of resorcinol comonomer into the PC backbone reduces unfavorable interaction energy between PC block and PET by factor of ~2: $\chi = 0.063$ for PC/PET vs. $\chi = 0.029$ for RPC20/PET.

Table 3
Calculated Flory–Huggins interaction parameter for PC/PET blends or RPC20/PET blends.

	PC/PET blends	RPC20/PET blends
M_w of PC or RPC20	30,000	31,500
Highest M_w of PET in miscible blends	2760	9520
Lowest M_w of PET in immiscible blends	4130	13200
Calculated Flory–Huggins interaction parameter, χ	$0.0548 < \chi < 0.0719$	$0.0265 < \chi < 0.0316$

4. Discussion

Previously, we [1] reported that an RPC copolymer with 80 mol% resorcinol phthalate (RPC80) and PET form miscible blends. Based on an empirical Nishi–Wang equation [32], the effective interaction parameter χ_{12} of −0.36 is extracted from the melting point depression and composition relationship. The negative χ_{12} for this blend system seems unusual as polycarbonate, one of the components in the RPC80 copolymer, is thermodynamically immiscible with PET [33,34]. Actually, the RPC/PET pair represents a class of blends of homopolymer A-copolymer B–C pairs, where B and C are repulsive and at least one of their corresponding homopolymers is immiscible with the homopolymer A [35–41]. For this type of blend, miscibility could be driven by the so-called "intramolecular repulsion" between the two components comprising the copolymer, even if a favorable specific interaction is not present. This may be better understood in the context of the following formula derived by Kambour et al. [35] based on Flory–Huggin's theory. In the case of PET (homopolymer A) and RPC (copolymer B_y–C_{1-y}) blends,

$$\chi_{\text{blend}} = y\chi_{AB} + (1-y)\chi_{AC} - y(1-y)\chi_{BC} \tag{5}$$

where χ_{blend} is the effective interaction parameter between PET and RPC that determines their miscibility, and χ_{AB}, χ_{AC} and χ_{BC} are interaction parameters between different combinations of polymer repeating units that contribute to the miscibility of the blends. Therefore, even when all three binary interaction parameters are all positive, if χ_{BC} is much greater than χ_{AB} or χ_{AC}, χ_{blend} can be a negative value at certain copolymer compositions. This may explain why χ_{blend} of −0.36 was obtained for the RPC80/PET blends. However, according to Equation (5), as the copolymer composition y varies, the miscibility window of the RPC/PET blends is expected to change. Specifically, a decrease of the resorcinol content y in the copolymer would lead to an increase of χ_{blend}, which would cause the blends to be less miscible. Ideally, if all the three binary interaction parameters in Equation (5) are available, the miscibility characteristics for the RPC/PET blends with different compositions in the copolymer RPC can be determined. However, from an application standpoint, the interaction parameters may not be readily available for most polymer pairs including poly(resorcinol phthalate)/PET. In contrast, solubility parameters can be estimated by group contribution methods. In the present study, the interaction parameters between polymers were approximated by an equation developed by Paul and Barlow [36].

$$B = RT\chi_{AB} = (\delta_A - \delta_B)^2 \tag{6}$$

where B is the binary interaction energy density, R is the gas constant, T is temperature, χ_{AB} is the Flory–Huggins interaction

Table 4
Solubility parameters calculated by Small's, Hoy's, Coleman's, and topological methods.

Method	Unit	PC	PET	Poly(resorcinol phthalate)
Small	$(\text{cal/cm}^3)^{0.5}$	9.7	10.7	11.0
Hoy	$(\text{cal/cm}^3)^{0.5}$	10.4	11.3	11.7
Coleman	$(\text{cal/cm}^3)^{0.5}$	10.4	11.5	12.1
Topological	$(\text{cal/cm}^3)^{0.5}$	10.3	11.1	11.3

Density and molar volume of amorphous phase (cm^3/g) were calculated by van Krevelen's method. Density of PC, poly(resorcinol phthalate), and PET are 1.2, 1.36, and 1.33 g/cm^3, respectively. Molar volumes of PC, poly(resorcinol phthalate), and PET are 254, 240, and 192 g/cm^3, respectively.

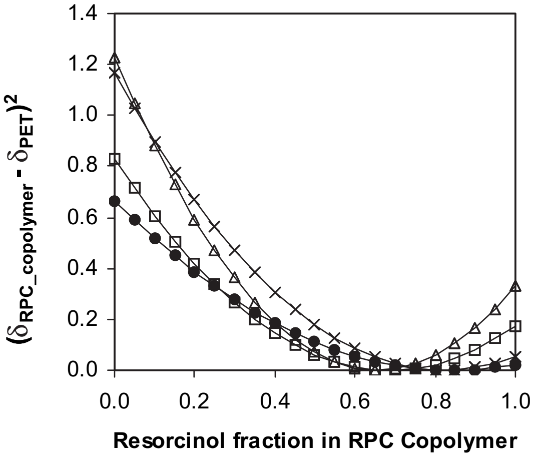

Fig. 9. Flory–Huggins interaction parameter (equivalent to *y*-axis) as a function of volume fraction of RP in RPC copolymer. The solubility parameter was calculated by Small's (×), Hoy (○), Coleman (❐), and Topological (●) group contribution methods.

parameter between polymer A and B, and δ_A and δ_B are the solubility parameters of polymer 1 and polymer 2, respectively. The equation (6) has a limitation that it cannot predict negative values of χ_{AB} but it is still useful to estimate similarity/miscibility of polymer pairs.

By combining equations (5) and (6) [36],

$$\chi_{\text{blend}} = [y\delta_B + (1-y)\delta_C - \delta_A]^2/RT = \left(\delta_{\text{RPC\_copolymer}} - \delta_{\text{PET}}\right)^2 /RT \text{where,} \;\; \delta_{\text{RPC\_copolymer}} \equiv y\delta_B + (1-y)\delta_C \qquad (7)$$

where A is the homopolymer (PET in the present study), B and C are comonomers in the copolymer, and y is the volume fraction of B in the copolymer.

Empirical calculations based on molar group contributions have been used to estimate solubility parameters by various methods, including Small [42], Hoy [43], and Coleman et al. [44]. More recently, Bicerano proposed "topological methods" to predict the solubility parameter of polymers [45]. Table 4 summarizes the solubility parameters for PC, PET, poly(resorcinol phthalate) by group contribution methods. All methods consistently support that the solubility parameters have the following order: Poly(resorcinol phthalate) > PET > PC.

Fig. 9 displays interaction parameters, $RT\chi_{\text{blend}}$, of PET and RPC copolymer as a function of volume fraction of resorcinol phthalate (RP) repeating unit in RPC copolymer based on the equation (7). The Fig. 9 implies that PET should have the most favorable interaction with RPC copolymers at a volume fraction of resorcinol of ~0.7. Numerical calculation for equation (7) provides minimum interaction parameter, i.e. 0, at an RP volume fraction of 0.82, 0.69, 0.66, or 0.85 based on Small's, Hoy's, Coleman's, and Topological method, respectively. In summary, these numerical and graphical solutions in combination with group contribution methods well agree with our experimental results on PET and RPC copolymers in the present study.

5. Conclusions

The phase behavior of the blends of PET and RPC and the blends of PET and PC was investigated by DMA, DSC, and TEM. High molecular weight PET and RPC copolymer with 20 mol% resorcinol phthalate (RPC20) showed two glass transition temperatures in DMA and DSC but the cold crystallization rate of PET phase was substantially lowered as compared to neat PET, indicating partially miscibility at all compositions. The RPC20 with $M_w = 31{,}500$ g/mol formed miscible blends with PET when PET has weight-average molecular weight <9500 g/mol. The Flory–Huggins interaction parameter between PET and RPC20 was calculated to be 0.029 ± 0.003 by using the Flory–Huggins equation at critical composition and molecular weight. In contrast, PC with $M_w = 30{,}000$ g/mol formed miscible blends with PET only when PET had molecular weight <2800 g/mol, indicating PC/PET blends was much less miscible than RPC20/PET blends. Group contribution methods agreed well with the experimental results obtained both in the present study and a previous study [1], predicting that the addition of a resorcinol phthalate block to a PC backbone should increase the miscibility of PC and PET.

Acknowledgments

The authors gratefully acknowledge Dr. David Zoller for GPC measurements and analysis, Mr. Eugene Galperin for NMR analysis, and Ms. Kim Paul for assistance with the DSC measurements. We also thank Dr. Jim Scobbo for his valuable suggestions on the manuscript.

References

[1] Kim SD, Chakravarti S, Tian J. Journal of Applied Polymer Science 2008;110(5):2623–33.
[2] Kong Y, Hay JN. Polymer 2002;43(6):1805–11.
[3] Nassar TR, Paul DR, Barlow JW. Journal of Applied Polymer Science 1979;23(1):85–99.
[4] Murff SR, Barlow JW, Paul DR. Journal of Applied Polymer Science 1984;29(11):3231–40.
[5] Kim WN, Burns CM. Journal of Polymer Science Part B: Polymer Physics 1990;28(9):1409–29.
[6] Wang L-H, Huang Z, Hong T, Porter RS. Journal of Macromolecular Science, Part B, Physics 1990;29(2&3):155–69.
[7] Suriano JA, Siclovan TM, Pickett JE, Brunelle DJ, O'Neil GA, Zhong H. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) 2003;44(1):748–9.
[8] Cojocariu G, Blubaugh C, Li X, Malinoski J, Sybert P. Annual Technical Conference – ANTEC, Conference Proceedings; 2005. p. 2528–32.
[9] Gallucci RR, Sanner M, Sybert P. Annual Technical Conference – ANTEC, Conference Proceedings; 2005. p. 2508–12.
[10] Sybert P, Klei S, Rosendale D, Di J, Shen D. Annual Technical Conference – ANTEC, Conference Proceedings; 2005. p. 2523–27.
[11] Small J, James D, Seymour RW, Flora TE. Eastman Kodak Company, U.S. Pat. 5,194,523; 1993.
[12] Hamilton DG, Gallucci RR. Journal of Applied Polymer Science 1993;48(12):2249–52.
[13] Devaux J, Godard P, Mercier JP, Touillaux R, Dereppe JM. Journal of Polymer Science: Polymer Physics Edition 1982;20(10):1881–94.
[14] Porter RS, Wang L-H. Polymer 1992;33(10):2019–30.
[15] Ellis TS. Polymer 1998;39(20):4741–9.
[16] Hopfe I, Pompe G, Eichhorn K-J. Polymer 1997;38(10):2321–7.
[17] Montaudo G, Puglisi C, Samperi F. Macromolecules 1998;31(3):650–61.
[18] Matsuda H, Asakura T, Nagasaka B, Sato K. Macromolecules 2004;37(12):4651–7.
[19] Donovan AR, Moad G. Polymer 2005;46(14):5005–11.
[20] Wunderlich B. Thermal analysis of polymeric materials. Berlin: Spinger; 2005.
[21] Kimura M, Porter RS, Salee G. Journal of Polymer Science: Polymer Physics Edition 1983;21(3):367–78.
[22] Fox J, Thomas G, Flory PJ. Journal of Applied Physics 1950;21(6):581–91.
[23] Fox TG, Flory PJ. Journal of Polymer Science 1954;14(75):315–9.
[24] Hintermeyer J, Herrmann A, Kahlau R, Goiceanu C, Rol̀ssler EA. Macromolecules 2008;41(23):9335–44.
[25] Agapov AL, Sokolov AP. Macromolecules 2009;42(7):2877–8.
[26] Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A. Macromolecules 2002;27(17):4639–47.
[27] Fox TG. Bulletin of the American Physical Society 1956;1:123.
[28] Flory PJ. Principles of Polymer Chemistry. Ithaca: Cornell University Press; 1953.
[29] Chen HY, Chum SP, Hiltner A, Baer E. Macromolecules 2001;34(12):4033–42.
[30] Sperling LH. Polymeric multicomponent materials: an introduction. New York: John Wiley & Sons, Inc.; 1997.
[31] Koningsveld R, Chermin HAG, Gordon M. Proceedings of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences 1970;319:331–49.
[32] Nishi T, Wang TT. Macromolecules 1975;8(6):909–15.

[33] Henrichs PM, Tribone J, Massa DJ, Hewitt JM. Macromolecules 1988;21(5):1282–91.
[34] Suzuki T, Tanaka H, Nishi T. Polymer 1989;30(7):1287–97.
[35] Kambour RP, Bendler JT, Bopp RC. Macromolecules 1983;16(5):753–7.
[36] Paul DR, Barlow JW. Polymer 1984;25(4):487–94.
[37] Xie R, Weiss RA. Polymer 1998;39(13):2851–8.
[38] Brinke GT, Karasz FE, MacKnight WJ. Macromolecules 1983;16(12):127–1832.
[39] Lu X, Weiss RA. Macromolecules 1996;29(4):1216–21.
[40] Zhou NC, Xu C, Burghardt WR, Composto RJ, Winey KI. Macromolecules 2006;39(6):2373–9.
[41] Aoki Y. Macromolecules 1988;21(5):1277–82.
[42] Small PA. Journal of Applied Chemistry 1953;3:71–80.
[43] Hoy KL. Journal of Paint Technology 1970;42(541):76–8. 115–118.
[44] Coleman MM, Graf JF, Painter PC. Specific interaction and the miscibility of polymer blends. Lancaster: Technomic Publishing; 1991.
[45] Bicerano J. Prediction of polymer properties. New York: Marcel Dekker Inc.; 2002.