

Compatibility behaviour of blends of poly(ethylene terephthalate) with an amorphous copolyester

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The compatibility behaviour of melt-mixed blends of an amorphous copolyester (poly(ethylene-cocyclohexane 1,4-dimethanol terephthalate), PETG) with poly(ethylene terephthalate) (PET), was investigated over the complete composition range. The techniques applied were dynamic mechanical analysis, tensile testing and differential scanning calorimetry. The effect of thermal history was also examined. In quenched blends tensile properties were good in all compositions. Suitable treatment of thermal data allowed the determination of the polymer–polymer interaction parameter χ_{12} whose value supports the view that the blend is miscible at increased PETG levels. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In a previous communication¹ the compatibility behaviour of poly(butylene terephthalate) (PBT) with an amorphous polyester, poly(ethylene-co-cyclohexane 1,4-dimethanol terephthalate) (PETG) was examined. Mechanical and morphology characterization techniques demonstrated that the system is miscible in the amorphous state. In this study the phase behaviour and properties of the related binary blend of poly(ethylene terephthalate) (PET)/PETG are reported. PET is a widely used engineering thermoplastic resin and at present new avenues are sought to absorb the large quantities available via recycling^{2,3}; its property diversi-fication by blending may provide such a route. PETG combines good toughness even at low temperatures with film clarity and melt strength. The last property may prove particularly useful in blends with ordinary PET which has low melt strength so that it may not be extrusion blow moulded with conventional equipment⁴.

A considerable number of crystalline/crystalline and crystalline/amorphous polyester blends have appeared in the literature and have been reviewed before¹ with reference to PBT. Blends with PBT were studied by Stein and coworkers^{5,6} and more recently by Avramova⁷ who confirmed miscibility in the amorphous state. PET/ polycarbonate (PC) blends⁸ exhibited a single T_g up to 50 wt% PC. At higher PC compositions phase separation occurred. In a more recent study Kim and Burns⁹ concluded that the binary mixture is not miscible on a microscopic scale. A related study¹⁰ of PET/PC modified with an elastomer, examined impact properties and the influence of primary and entanglement molecular weights of the matrix polymer. Yoon *et al.*¹¹ examined

the competition between phase separation and transesterification reactions and their influence on morphological features of PET/PC blends. The reactions occurring during thermal processing and pyrolysis of PET/PC blends were investigated by mass spectrometry¹². In these blends copolymers formed by ester exchange reactions during melt mixing were isolated with thin layer chromatography (t.l.c.) and identified by infra-red (i.r.) spectroscopy¹³.

PET/polyarylate (PAr) blends, based on bisphenol-A, were studied by Robeson¹⁴. Ester exchange leading to single phase behaviour occurs with moderate temperature and mixing time. More recent studies covered the rheological behaviour of these blends¹⁵ and the suppressing action of organophosphites on the ester-exchange reactions¹⁶. The *in situ* compatibilization via catalysed transesterification of PETG/poly(ethylene-*co*-vinyl acetate) (EVA) was examined by Legros *et al.*¹⁷ using mechanical, rheological and morphological characterization techniques. Blends of PET with poly(ethylene 2,6-naphthalene carboxylate) (PEN) were compatibilized via transesterification and various reaction parameters were determined¹⁸.

Further studies on this system dealing with miscibility, transesterification and crystallization were reported by Zachmann and Andresen¹⁹. Miscibility of PET/PEN and of PET/copolyesters with *p*-hydroxy benzoic acid (PHB) was also investigated using solid state nuclear magnetic resonance $(n.m.r.)^{20}$.

Numerous papers have appeared on PET blended with liquid crystalline polyesters (LCP). The reasons as to why blends containing LCP gained considerable importance are explained by Brown and Alder in their recent review²¹. Mechanical properties, morphology and interfacial adhesion studies were reported by Shin and coworkers^{22,23} on PET/semiflexible thermotropic LCP (TLCP). The feasibility of introducing a TLCP as a

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compatibilizer in order to improve the adhesion of PET/LCP blends was investigated^{24,25}. Perkins *et al.*²⁶ reported on the morphology and rheology of PET/TLCP ('Vectra A') blends at several compositions. 'Vectra A' is a block copolymer of poly(2-hydroxy-6-naphthoic acid) and poly(*p*-hydroxy benzoic acid).

Several PET blends appeared in the patent litemature and Utracki lists several of them in his recent monograph²⁷. Most of these combine PET with PC or PBT, with the addition of impact modifiers, e.g. ABS, modified olefin copolymer (EPDM) and acrylic resins.

In the present work the miscibility behaviour of meltmixed blends of PETG/PET covering the complete composition range was characterized using dynamic mechanical analysis (d.m.a.), tensile testing and differential scanning calorimetry (d.s.c.). The effect of thermal treatment on mechanical behaviour and thermal properties was also examined.

EXPERIMENTAL

Materials and specimen preparation

PET was extrusion grade obtained from Akzo b.v. (Arnite DO_z 300). It was reported to have predominantly terminal hydroxy groups, an $\overline{M}_n = 23500 \text{ g mol}^{-1}$. $T_m = 252^{\circ}\text{C}$ and an amorphous product density of 1.34 g cm⁻³. PETG-6763 from Tennessee Eastman Co.. with $\overline{M}_n = 26000 \text{ g mol}^{-1}$ was utilized. It was reported¹⁴ to consist of cyclohexane dimethanol, ethylene glycol and terephthalic acid in a molar ratio of approximately 1/2/3. They were both dried at 80°C for 12 h *in vacuo*. Blends were prepared by melt mixing at 265°C using a CSI Lab mixing extruder (model CS—194 AV) at 100 rpm. Time of mixing was *ca* 0.5 min. Compositions prepared were 12/88, 25/75, 50/50, 75/25, 88/12 (w/w).

Films were compression moulded between Teflon sheets at 265°C and 5 MPa and quenched to 0° C. Blends were examined after annealing at 150°C for 1 h.

Apparatus and procedures

D.s.c. measurements were carried out in an inert atmosphere using a DuPont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was carried out with an indium standard. The sample weight was 10 mg and the heating rate was 20° C min⁻¹. The heating cycle applied was 25° C $\rightarrow 270^{\circ}$ C (2 min) $\rightarrow 25^{\circ}$ C $\rightarrow 270^{\circ}$ C. Thermal data were obtained during the second heating run.

Tensile tests were performed according to ASTM D 882 at 23°C using a J.J. Tensile Tester type T 5001 and film strips with dimensions $6.0 \times 0.65 \times 0.025$ cm³. Data reported were obtained at a crosshead speed of 10 cm min^{-1} . Tensile tests were repeated five to eight times and the values as well as stress strain curves reported are the average of these tests.

The d.m.a. data, loss tangent $\tan \delta$ and complex modulus $|E^*|$ were obtained at 110 Hz using the direct reading viscoelastometer (Rheovibron model DDV II-C) and a heating rate of $ca 2^{\circ}$ C min⁻¹. Specimen dimensions were $3.0 \times 0.2 \times 0.02$ cm³.

RESULTS

Dynamic mechanical properties

These are summarized in *Figures 1–3* and in *Table 1*.



Figure 1 Thermomechanical spectra of quenched PET/PETG blend: $(0,0/100; 0.50/50; \blacksquare, 100/0)$



Figure 2 Temperature dependence of loss modulus E'' of annealed PET/PETG blends: \diamond , 0/100; ----, 50/50; ---, 75/25; \diamond , 100/0

The glass transition temperature (T_g) relaxation of PETG at ca 94°C is observed at about the same temperature (93°C) where the main relaxation (α) of amorphous PET is located²⁸. A low temperature relaxation (β) at $ca - 50^{\circ}$ C is detected for PET and PETG also. Consequently in the 50/50 (w/w) blend, a single T_{gb} (E' max) is observed, see Figure 1, at the same temperature where the T_{gs} of pure components are located. Since no peak differentiation could be detected among blends and pure components, no d.m.a. results for other quenched blends are reported. It is documented in the literature²⁹ that annealing causes a considerable T_g shift upwards of PET due to crystallization. If PETG is miscible with the amorphous phase of PET then the blends would give rise to a new peak intermediate between the pure component relaxations. Figures 2 and 3 give the thermomechanical spectra of the 50/50 and 75/25 blends and of the pure

components after annealing for 1 h at 150°C. The results in Figure 2 confirm that the $T_{\rm gb}$ of the blends, located at intermediate temperatures, is what would be approximately expected for a miscible blend at these compositions. The increase in width and the decrease of the relaxation strength of the blends is attributed to the influence of the crystalline PET phase. The inset in Figure 3 compares the prediction of $T_{\rm gb}$ according to the Fox equation with the experimental values.

Thermal properties

Thermal transitions and crystallinity data are also reported in *Table 1*. There is a significant $T_{\rm mb}$ depression, the largest being 15°C for the 50/50 and the 25/75 blends.



Figure 3 Temperature dependence of storage modulus E' of annealed PET/PETG blends: \diamond , 0/100; ----, 50/50; ---, 75/25; \blacklozenge , 100/0. Inset: Comparison of experimental T_{gb} with the prediction of Fox equation, $1/T_{gb} = w_1/T_{g1} + w_2/T_{g2}$

Table 1 Viscoelastic and t	hermal prop	perties of	blends
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The considerable $T_{\rm m}$ depression led us to investigate the possibility that blend components may be miscible in the melt, and so determine the thermodynamic interaction parameter χ_{12} . To separate the morphological and thermodynamic factors, the Hoffman–Weeks procedure³⁰ was applied by plotting $T_{\rm mb}$ (experimental melting points) versus $T_{\rm c}$ (annealing temperature) for all compositions. This analysis is based on the relation

$$T_{\rm mn} = T_{\rm mb}^0 \left(1 - \frac{1}{\eta} \right) + \frac{T_{\rm c}}{\eta} \tag{1}$$

and yields the equilibrium T_m of PET in the blend (T_{mb}^0) and in the pure state (T_m^0) , also included in *Table 1*. A lamellar thickening factor η may also be obtained relating the final crystal thickness l_c to the initial l^* , i.e. $l_{\rm c} = \eta l^*$. Plots based on equation (1) are shown in *Figure* 4. Annealing temperatures were not extended beyond ca 210°C since it was observed that annealing beyond this temperature led to a significant $T_{\rm mb}$ drop, out of line with the rest of data. This could be the result of chemical reaction (possibly transesterification) taking place during prolonged heating at temperatures $T > 210^{\circ}$ C. A PET crystallization exotherm during the d.s.c. heat scan was observed and its onset temperature T_{ons} (see Table 1), is depressed with increasing PETG content. This is also the case for the PBT/PETG blend¹ and suggests that crystallization is facilitated in the presence of PETG. This helps explain the composition dependence of PET crystallinity in the blend (see *Table 1*). During the heat scan of quenched blends, PET develops a higher amount of crystallinity in the viscoelastic matrix of PETG. In these specimens its crystallinity is approximately constant and higher than that of pure PET. In annealed blends crystallinity development is also favoured in the presence of PETG but in this case, in more dilute systems (low PET contents), it is possible that diffusional processes are facilitated and higher crystallinity develops. An enhancement of PBT crystallinity in PBT/PAr blends was also reported by Kimura and Porter³¹ with the addition of up to 40 wt% PAr. Nadkarni³² reported a

PET/PETG ^c	$T_{\rm gh}, E_{\rm max}''$ (°C)		Crystallinity % PET [#]		Crystallinity % blend					0
	α	β	Quenched	Annealed	Quenched	Annealed	$T_{gb}^{\ a}$ (°C)	T_{mb} (°C)	T _{ons} (°C)	<i>T</i> ⁰ _{mb} (°C)
100/0	93	-50	3 ^c	21 ^{<i>d</i>}	3 ^c	21 ^{<i>d</i>}	80	250	165	280
$100/0^{d}$	117	_								
88/12	_	-	11	21	9	19	80	250	165	_
75/25	_	-	9	30	7	22	80	245	165	272 ± 3
75/25 ^d	108									
50/50	93.3	-49	7	38	4	19	80	235	160	274 ± 4
$50/50^{d}$	100	-								
25/75	_	-	6	38	2	9	80	235	155	270 ± 3
12/88	-	-	8	51	1	6	80	240	-	266 ± 3
0/100	94	-43	0	0	0	0	80		-	-
$0/100^{d}$	95	-								

^{*a*} From d.s.c.

 $^{b}\Delta H_{\rm f} = 33.5\,{\rm cal\,g^{-1}}$

Quenched blends, except where noted

^d Annealed blends

crystallinity enhancement of PET in the presence of a high T_g amorphous polyester (PMMA), a system bearing similarity to the present blend. No explanation based on available theory was offered.

In ref. 32 a PET/polyester (Kodar A 150) was quoted as a PET/PETG blend. Kodar A 150 a cyclohexane dimethanol-tere/isopthalic acid copolymer¹⁴ has a different structure and different physical constants: a much higher T_g than PETG, it is semicrystalline while PETG is amorphous whether in the quenched or annealed state. Thus reported³² results cannot be compared with our findings.

These considerations also help explain the composition dependence of total blend crystallinity if the dilution factor caused by the amorphous PETG is also taken into account.

Tensile properties

Stress-strain $\sigma - \varepsilon$ data of quenched blends are depicted in *Figure 5* and tensile properties are summarized in *Table 2*. Ultimate properties, strength σ_b and



Figure 4 Hoffman Weeks plots of PET/PETG blends: ■. 12/88; □. 25/75; ○. 50/50; ●. 75/25

elongation ε_b are excellent at all compositions. Annealing raises σ_b due to PET crystallization but drastically reduces ultimate elongation due to embrittlement. In the context of blend compatibility, ε_b is a very sensitive indicator of component adhesion, for mechanically compatible systems, or cohesion, for miscible blends³³. Thus tensile properties of quenched blends in this work indirectly support the view that the system is mechanically compatible or miscible. The energy to tensile failure E_b obtained as the area under the stress-strain curve, see *Figure 6*, shows similar trends in quenched blends. Annealing lowers E_b , since the amorphous phase 'binding' both components is reduced.

DISCUSSION

Experimental evidence from d.m.a., large deformation mechanical behaviour as well as thermal data, suggests that the blend is miscible in the amorphous phase. Since a significant T_m depression was observed in blends, relevant data obtained using the Hoffman– Weeks procedure (see equation (1)) were analysed to obtain the χ_{12} interaction parameter. The working



Figure 5 Stress-strain properties of quenched PET/PETG blends: , 100/0; 0, 75/25; ---, 50/50; ---, 25/75; ---, 0/100. Inset: annealed blends at indicated compositions

		Quenched			Annealed		
	$\sigma_{\rm b}$	ć h	$\mathcal{E}_{\mathbf{b}}$	$\sigma_{\rm b}$	ੰh	$E_{\rm b}$	
PET/PETG	(MPa)	(⁰ .ზ.)	$(J \text{ cm}^{-3})$	(MPa)	(%)	$(J \text{ cm}^{-3})$	
100/0	49 ± 2	395 ± 40	102	66 ± 2	18 ± 7	7	
88/12	$.39 \pm 2$	445 ± 75	110	51 ± 4	9 ± 2	6	
75/25	37 ± 2	466 ± 65	124	56 ± 3	11 ± 1	3	
50/50	36 ± 3	460 ± 35	122	30 ± 3	100 ± 40	30	
25/75	31 ± 2	415 ± 35	116	30 ± 4	112 ± 40	32	
12/88	37 ± 4	423 ± 70	106	40 ± 5	298 ± 40	27	
0/100	46 ± 3	390 ± 38	122	46 ± 3	390 ± 38	122	
50/50 25/75 12/88 0/100	36 ± 3 31 ± 2 37 ± 4 46 ± 3	$460 \pm .35$ $415 \pm .35$ $423 \pm .70$ $390 \pm .38$	122 116 106 122	30 ± 3 30 ± 4 40 ± 5 46 ± 3	100 ± 40 112 ± 40 298 ± 40 390 ± 38	30 32 27 122	

Table 2 Tensile properties of blends



Figure 6 Composition dependence of energy to tensile failure E_b of quenched blends (**II**); open symbols annealed blends

equation is given³⁴ by

$$\left(\frac{1}{T_{\rm mb}^0} - \frac{1}{T_{\rm m}^0}\right)\frac{1}{\varphi_2} = -\frac{R \cdot \bar{V}_{\rm lu}}{\Delta H_{\rm f}^0 \cdot \bar{V}_{\rm 2u}}\chi_{12}\varphi_2 \qquad (2)$$

where \bar{V}_{iu} is the molar volume of repeat unit *i*, and φ_i is the volume fraction of polymer *i*; indices 1 and 2 refer to the crystalline and amorphous (PETG) component in the blend respectively, and ΔH_f^0 is the heat of fusion of the perfect crystal taken³⁵ as $\Delta H_f^0 = 140 \text{ J g}^{-1}$. For the T_m^0 the value adopted was taken from ref. 36.

Application of equation (2) assumes that there are no entropic contributions to the $T_{\rm mb}$ depression, and that χ_{12} is composition independent. Morphological effects may also influence $T_{\rm mb}$. The first assumption is valid for high molecular weight of blend components. It is now recognized that the second assumption may be assumed valid as a first approximation^{34,37}. Morphological effects are expected to be eliminated using the Hoffman-Weeks procedure to determine T_{mb}^0 . However, as explained by Runt *et al.*³⁸ the extrapolation procedure may introduce some error in the quantity of interest (χ_{12}). Using the linear portion of the plot of equation (2) and interpolating between experimental points (see Figure 7a), one obtains $\chi_{12} = -0.12$ at $T_m^0 = 280^{\circ}$ C and essentially a zero intercept value (2.2×10^{-5}) . If all four points are used, $\chi_{12} = 0.29$ and also there is a negligible intercept (1.1×10^{-4}) . We propose that the former negative χ_{12} value should be adopted on the basis of the following experimental evidence: (i) A positive χ_{12} value would not lead to a $T_{\rm mb}$ depression; (ii) d.m.a. indicates segmental miscibility, indirectly supported by the tensile properties; (iii) approximate χ_{12} calculation yields a near zero (0.003) value at melt temperatures (see below); (iv) a small negative χ_{12} value indicating weak intermolecular π -electron interactions³¹ is expected for the present system by analogy to PET/PBT^7 and $PBT/PETG^1$ blends.

In their study of PBT/PAr blends, a system bearing analogy to PET/PETG, Huo and Cebe³⁹ reported a significant composition dependence of χ_{12} whose value ranged from -0.65 to -0.22. Gallagher *et al.*⁴⁰ calculated



Figure 7 Determination of interaction parameter χ_{12} of blends: (a) using equation (2), ---, all points; ----, deleting point at $\varphi_2 = 0.248$. (b) Using equation (3)

a value of $\chi_{12} < 0.04$ for miscible PBT/poly(ether ester) blends. The small deviation from the straight line introduced by the 75/25 composition ($\varphi_2 = 0.248$) should be attributed to the composition dependence of χ_{12} and ultimately to the inadequacy of pertinent theory^{37,41}.

To confirm that the entropic factor is negligible, hence the application of equation (2) valid, data were also analysed using the complete equation proposed by Nishi and Wang³⁴.

$$\frac{\Delta H_{\rm f}^{0} V_{2\rm u}}{\bar{V}_{1\rm u}} \left(\frac{1}{T_{\rm mb}^{0}} - \frac{1}{T_{\rm m}^{0}}\right) + \frac{\ln\varphi_1}{m_1} + \left(\frac{1}{m_1} - \frac{1}{m_2}\right)\varphi_2 = -\chi_{12}\varphi_2 \tag{3}$$

where m_1 is the degree of polymerization of component *i*. A plot of equation (3) gave as slope $\chi_{12} = -0.09$ and a non-zero intercept value of 0.07; see Figure 7b. Since morphological effects were minimized (by using T_{mb}^0 values), this small positive value should be attributed to the composition dependence of χ_{12} and/or to molecular weight effects. These results show that the molecular weight has a negligible effect on χ_{12} .

Data were also analysed using the Kwei-Frisch⁴² equation (4) which may be useful to assess the influence of morphological factors and of molecular weight on $T_{\rm mb}$

depression and in principle avoids the necessity of using T_{mb}^{0} (i.e. the Hoffman–Weeks procedure)

$$\frac{\Delta H_{\rm f}^0(T_{\rm m}^0 - T_{\rm mb})}{\varphi_2 R T_{\rm m}^0} - \frac{T_{\rm mb}}{m_2} - \frac{\varphi_2 T_{\rm mb}}{2m_1} = \frac{C}{R} - \beta \varphi_2 \qquad (4)$$

where C is a proportionality constant due to morphological contributions and $\beta = \chi_{12}T_{\rm mb}$. A plot of the lefthand side vs φ_2 should give a straight line whose slope yields χ_{12} . Use of our $T_{\rm mb}$ data gave $\chi_{12} = 1.71$ and C = 2002. If the point at $\varphi_2 = 0.248$ is deleted, $\chi_{12} =$ 1.35 and C = 1722. Use of $T_{\rm mb}^0$ data gave $\chi_{12} = 0.26$ and C = 372. Omitting the point at $\varphi_2 = 0.248$ one obtains $\chi_{12} = -0.10$ and C = 68 for all $T_{\rm mb}$.

The high positive χ_{12} values should be rejected for the reasons given before. The *C* value indicates the presence of morphological effects when $T_{\rm mb}$ data are used.

The availability of T_{mb}^{0} data induced us to use them and as expected the morphological factor is considerably reduced and the χ_{12} value agrees with previous findings. However, it is suggested that the intended purpose of relationship (4) was to use T_{mb} data thus avoiding the Hoffman–Weeks procedure, or in cases where annealing at T_{mb} could lead to polymer degradation⁴³. The conclusion of this analysis points out that the Hoffman–Weeks procedure can minimize morphological effects and that the complete equation (3) in using all experimental data has an edge over the other relationships. In the present case the result of the φ_2 being raised to the second power, thus giving a smaller weight to low concentrations of component 2, minimizes the anomaly shown by the 75/25 blend when using equations (2) or (4).

To further rationalize results, the copolymer -copolymer miscibility scheme⁴⁴ which takes into account interas well as intramolecular forces was applied. For a binary blend of a homopolymer of units A_n with a random copolymer $(A_yC_{1-y})_m$, both of high molecular weight. miscibility is predicted depending on the sign of the quadratic function f(y) identified in the present case with χ_{12} .

$$\chi_{12} = (1 - r)^2 \chi_{AC}$$
 (5)

where y is the copolymer composition in volume fraction and χ_{AC} the segmental interaction parameter between structural units A and C (PETG).

In expression (5) miscibility is predicted for copolymer compositions where $\chi_{12} = 0$. For the present system A is identified as the PET repeat unit and A_v , C_{1-v} as



and

$$\begin{bmatrix} \mathbf{O} & \mathbf{O} \\ \| & \| \\ -\mathbf{O}\mathbf{C}\mathbf{H}_2 - \mathbf{O} - \mathbf{C} - \mathbf{O} - \mathbf{C} \end{bmatrix}_{0.33}$$

respectively. The segmental interaction parameter χ_{AC} may be determined according to Krause's scheme⁴⁵ using equation (6) and solubility parameter values which may also be obtained by calculation using equation (7)

$$\chi_{\rm AC} = \frac{V_{\rm r}}{RT} (\delta_{\rm A} - \delta_{\rm C})^2 \tag{6}$$

$$\delta = \rho \frac{\Sigma F_{\rm i}}{M} \tag{7}$$



Figure 8 Effect of PETG structure on the interaction parameter χ_{12} at various temperatures; see text

where V_r is a reference volume, δ_A , δ_C the solubility parameter for structural units A and C, respectively, ρ is density, F_i group molar attraction constant and M the molecular weight of the repeat unit. For the copolymer, δ was calculated taking into account the ratio of basic units from which it may be assumed to be derived⁴⁵. Calculation of χ_{AC} using these concepts is valid since no strong specific forces are involved.

The results of such a calculation are given in Figure 8 in terms of the copolymer composition dependence of χ_{12} . The χ_{12} value obtained is very small: $\chi_{12} \approx 0.003$ for the particular copolymer composition (y = 0.67) at the mixing temperature employed (265°C). As expected χ_{12} is decreased, hence miscibility of the two components is favoured, as the proportion of PET unit in the copolymer is increased. The results also indicate that mixing is facilitated at high temperatures. Calculations of χ_{AC} , hence of χ_{12} , at different temperatures was made by combining equation (6) with the expression⁴⁶ $\partial \ln \delta / \partial T = -\alpha$, relating solubility parameter with the coefficient of cubic expansion α .

Data used in previous calculations are as follows. For the coefficient of thermal expansion, the value of amorphous PET was adopted⁴⁷ for PETG; $\alpha_{gPET} = \alpha_{gPETG} = 2.16 \times 10^{-4} \,^{\circ}\text{C}^{-1}$. Above T_g use was made of the Simha-Boyer rule⁴⁷ ($\alpha_1 - \alpha_g$) $T_g = 0.115$ to obtain α_1 ; $\alpha_{1PET} = \alpha_{1PETG} = 1.47 \times 10^{-3} \,^{\circ}\text{C}^{-1}$. Calculated solubility parameters at room temperature were $\delta_{PETamorphous} = 11.38$ (cal cm⁻³)^{1/2}, $\delta_{PETused} = 11.41$ (cal cm⁻³)1/2, $\delta_{PETG} = 10.71$ (cal cm⁻³)^{1/2}. Molar volumes are: $V_{PET} = 144 \,\text{cm}^3 \,\text{gmol}^{-1}$ adopted as V_r , $V_{PETG} = 163 \,\text{cm}^3 \,\text{gmol}^{-1}$. ρ (PETG calculated)⁴⁸ = 1.383 g cm⁻³ at 25° C. ρ (amorphous PET)⁴⁷ = 1.330 g cm⁻³ and ρ (crystal PET)⁴⁷ = 1.455 g cm⁻³ at 25° C. To calculate φ_2 the percentage crystallinity of PET was taken into account; see *Table 1*.

CONCLUSIONS

Melt-mixed PET/PETG blends show good mechanical properties at all compositions when quenched. Annealing

causes tensile properties reduction at high PET contents due to embrittlement. Indirect evidence from d.m.a., d.s.c. and the value of χ_{12} obtained from treatment of thermal data, support the view that the amorphous blend components are miscible at high PETG ($\varphi \ge 0.50$) contents. This is corroborated by the copolymer–copolymer miscibility prediction scheme.

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