

# **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  $\chi_{12}$  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 communication<sup>1</sup> 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<sup>2,3</sup>; its property diversification 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 equipment<sup>4</sup>.

A considerable number of crystalline/crystalline and crystalline/amorphous polyester blends have appeared in the literature and have been reviewed before<sup>1</sup> with reference to PBT. Blends with PBT were studied by Stein and coworkers<sup>3,6</sup> and more recently by Avramova<sup>7</sup> who confirmed miscibility in the amorphous state. PET/ polycarbonate (PC) blends<sup>8</sup> exhibited a single  $T<sub>g</sub>$  up to 50 wt% PC. At higher PC compositions phase separation occurred. In a more recent study Kim and Burns<sup>9</sup> concluded that the binary mixture is not miscible on a microscopic scale. A related study  $10^{10}$  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 spectrometry<sup>12</sup>. 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.) spectroscopy<sup>13</sup>.

PET/polyarylate (PAr) blends, based on bisphenol-A, were studied by  $Robeson<sup>14</sup>$ . Ester exchange leading to single phase behaviour occurs with moderate temperature and mixing time. More recent studies covered the rheological behaviour of these blends 15 and the suppressing action of organophosphites on the ester-exchange reactions<sup>16</sup>. 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 determined<sup>18</sup>.

Further studies on this system dealing with miscibility, transesterification and crystallization were reported by<br>Zachmann and Andresen<sup>19</sup>. 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 review<sup>21</sup>. Mechanical properties, morphology and interfacial adhesion studies were reported by Shin and coworkers<sup>22,23</sup> 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  $\text{PET}/\text{LCP}$  blends was investigated  $24.25$ . Perkins et al.<sup>26</sup> 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 litematurc and Utracki lists several of them in his recent mono $graph<sup>27</sup>$ . 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  $DO<sub>2</sub>$  300). It was reported to have predominantly (Arnite DO<sub>2</sub> 500). It was reported to the present of terminal hydroxy groups, an  $\overline{M}_n = 23,500$  g mol<sup>-1</sup>.  $T_{\text{m}} = \frac{3}{2}$  $252^{\circ}$ C and an amorphous product density of 1.34 g cm PETG-6763 from Tennessee Eastman Co.. with  $M_{\rm n} = 26000$  g mol<sup>-1</sup> was utilized. It was reported<sup>14</sup> 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  $265^{\circ}$ C and 5 MPa and quenched to  $0^{\circ}$ C. Blends were examined after annealing at  $150^{\circ}$ 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  $20^{\circ}$ C min<sup>-1</sup>. The heating cycle applied was  $25^{\circ}\text{C} \rightarrow 270^{\circ}\text{C}$  (2 min)  $\rightarrow 25^{\circ}\text{C}$  -270°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  $6.0 \times 0.65 \times 0.025$  cm<sup>3</sup>. Data reported were obtained at a crosshead speed of 10cm min<sup>-1</sup>. 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<sup>-1</sup>. Specimen dimensions were  $3.0 \times 0.2 \times 0.02$  cm<sup>3</sup>.

#### RESULTS

*Dynamic mechanical properties* 

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



Figure 1 Thermomechanical spectra of quenched PET/PETG blend:  $0.0100$ : 50/50;  $\blacksquare$ , 100/0



Figure 2 Temperature dependence of loss modulus  $E''$  of annealed **PET/PETG blends:**  $\Diamond$ ,  $0/100$ ;  $\_\_$ ,  $50/50$ ;  $\_\_$ ,  $75/25$ ;  $\blacklozenge$ ,  $100/0$ 

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 ( $\alpha$ ) of amorphous PET is located<sup>28</sup>. A low temperature relaxation ( $\beta$ ) at ca -50°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 l,* at the same temperature where the  $T_{\rm g}$ s 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 literature  $29$ 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  $T_{gb}$  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  $T_{gb}$  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:  $-$ , 50/50;  $-$  -  $-$ , 75/25;  $\blacklozenge$ , 100/0. Inset: Comparison of experimental  $T_{gb}$  with the prediction of Fox equation,  $1/T_{\text{gb}} = w_1/T_{\text{gl}} + w_2/T_{\text{g2}}$ 



The considerable  $T<sub>m</sub>$  depression led us to investigate the possibility that blend components may be miscible in the melt, and so determine the thermodynamic interaction parameter  $\chi_{12}$ . To separate the morphological and thermodynamic factors, the Hoffman-Weeks procedure<sup>30</sup> was applied by plotting  $T_{\rm mb}$  (experimental melting points) *versus*  $T_c$  (annealing temperature) for all compositions. This analysis is based on the relation

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

and yields the equilibrium  $T_{\rm m}$  of PET in the blend  $(T_{\rm mb}^{\rm o})$ and in the pure state  $(T_m^0)$ , also included in *Table 1*. A lamellar thickening factor  $\eta$  may also be obtained relating the final crystal thickness  $l_c$  to the initial  $l^*$ , i.e.  $l_c = \eta l^*$ . 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  $T_{\text{ons}}$  (see *Table 1*), is depressed with increasing PETG content. This is also the case for the PBT/PETG blend<sup>1</sup> 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 Porter<sup>31</sup> with the addition of up to 40 wt% PAr. Nadkarni<sup>32</sup> reported a



<sup>a</sup> From d.s.c.

 $h^{b} \Delta H_{f} = 33.5 \text{ cal g}^{-1}$ 

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 copolymer<sup>14</sup> 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 reported<sup>32</sup> 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  $\sigma = \epsilon$  data of quenched blends are depicted in *Figure 5* and tensile properties are summarized in *Table 2*. Ultimate properties, strength  $\sigma_{\rm b}$  and



**Figure 4** Hoffman Weeks plots of PET/PETG blends: **II.** 12/88;  $\Box$ , 25/75; O, 50/50;  $\bullet$ , 75/25

elongation  $\varepsilon_b$  are excellent at all compositions. Annealing raises  $\sigma_b$  due to PET crystallization but drastically reduces ultimate elongation due to embrittlement. In the context of blend compatibility,  $\varepsilon_b$  is a very sensitive indicator of component adhesion, for mechanically compatible systems, or cohesion, for miscible blends<sup>33</sup>. 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  $E<sub>b</sub>$  obtained as the area under the stress-strain curve, see *Figure 6*, shows similar trends in quenched blends. Annealing lowers  $E<sub>b</sub>$ , 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  $T<sub>m</sub>$  depression was observed in blends, relevant data obtained using the Hoffman Weeks procedure (see equation (1)) were analysed to obtain the  $\chi_{12}$  interaction parameter. The working



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



#### Table 2 Tensile properties of blends



Figure 6 Composition dependence of energy to tensile failure  $E<sub>b</sub>$  of quenched blends (**M**); open symbols annealed blends

equation is given  $34$  by

$$
\left(\frac{1}{T_{\rm mb}^0} - \frac{1}{T_{\rm m}^0}\right) \frac{1}{\varphi_2} = -\frac{R \cdot \bar{V}_{1u}}{\Delta H_1^0 \cdot \bar{V}_{2u}} \chi_{12} \varphi_2 \tag{2}
$$

where  $\bar{V}_{i\mu}$  is the molar volume of repeat unit *i*, and  $\varphi_i$  is the volume fraction of polymer  $i$ ; indices 1 and 2 refer to the crystalline and amorphous (PETG) component in the blend respectively, and  $\Delta H_{\rm f}^0$  is the heat of fusion of the perfect crystal taken<sup>35</sup> as  $\Delta H_f^0 = 140 \text{ J g}^{-1}$ . For the  $T_{\text{m}}^0$ 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  $\chi_{12}$  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  $T_{\rm mb}^0$ . However, as explained by Runt *et al. 38* the extrapolation procedure may introduce some error in the quantity of interest  $(\chi_{12})$ . 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  $T_m^{\prime\prime} = 280^{\circ}$ C and essentially a zero intercept value  $(2.2 \times 10^{-5})$ . If all four points are used,  $\chi_{12} = 0.29$  and also there is a negligible intercept  $(1.1 \times 10^{-4})$ . We propose that the former negative  $\chi_{12}$ value should be adopted on the basis of the following experimental evidence: (i) A positive  $\chi_{12}$  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  $\chi_{12}$  calculation yields a near zero (0.003) value at melt temperatures (see below); (iv) a small negative  $\chi_{12}$  value indicating weak intermolecular  $\pi$ -electron interactions<sup>31</sup> is expected for the present system by analogy to  $PET/PBT^7$  and  $PBT/PETG<sup>1</sup>$ blends.

In their study of PBT/PAr blends, a system bearing analogy to PET/PETG, Huo and Cebe<sup>39</sup> reported a significant composition dependence of  $\chi_{12}$  whose value ranged from  $-0.65$  to  $-0.22$ . Gallagher *et al.*<sup>40</sup> calculated



Figure 7 Determination of interaction parameter  $\chi_{12}$  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  $\chi_{12}$  and ultimately to the inadequacy of pertinent theory<sup>37,41</sup>.

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  $Wang<sup>34</sup>$ .

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

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  $T_{\text{mb}}^0$ values), this small positive value should be attributed to the composition dependence of  $\chi_{12}$  and/or to molecular weight effects. These results show that the molecular weight has a negligible effect on  $\chi_{12}$ .

Data were also analysed using the Kwei-Frisch<sup>42</sup> equation (4) which may be useful to assess the influence of morphological factors and of molecular weight on  $T_{\text{mb}}$  depression and in principle avoids the necessity of using  $T_{mb}^0$  (i.e. the Hoffman–Weeks procedure)

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

where  $C$  is a proportionality constant due to morphological contributions and  $\beta = \chi_{12}T_{\text{mb}}$ . A plot of the lefthand side vs  $\varphi_2$  should give a straight line whose slope yields  $\chi_{12}$ . Use of our  $T_{mb}$  data gave  $\chi_{12} = 1.71$  and  $C = 2002$ . If the point at  $\varphi_2 = 0.248$  is deleted,  $\chi_{12} = 1$ 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  $\tilde{C} = 68$  for all  $T_{\text{mb}}$ .

The high positive  $\chi_{12}$  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  $T_{\rm mb}^0$  data induced us to use them and as expected the morphological factor is considerably reduced and the  $\chi_{12}$  value agrees with previous findings. However, it is suggested that the intended purpose of relationship (4) was to use  $T_{\rm mb}$  data thus avoiding the Hoffman–Weeks procedure, or in cases where annealing at  $T_{\rm mb}$  could lead to polymer degradation<sup>43</sup>. 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  $\varphi_2$  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 scheme<sup>44</sup> 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  $(A_rC_{1-r})_m$ , both of high molecular weight. miscibility is predicted depending on the sign of the quadratic function  $f(y)$  identified in the present case with  $\chi_{12}$ .

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

where  $y$  is the copolymer composition in volume fraction and  $\chi_{AC}$  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

$$
\begin{bmatrix} 0 & 0 \\ \parallel & \parallel \\ -OCH_2 - \bigcirc -CH_2 - O - C - \bigcirc - \bigcirc - C - \parallel \\ 0.33 & 0.33 \end{bmatrix}
$$

respectively. The segmental interaction parameter  $\chi_{AC}$ may be determined according to Krause's scheme<sup>45</sup> using equation (6) and solubility parameter values which may also be obtained by calculation using equation (7)

$$
\chi_{AC} = \frac{V_r}{RT} (\delta_A - \delta_C)^2
$$
 (6)

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



**Figure 8** Effect of PETG structure on the interaction parameter  $\chi_1$ , at various temperatures; see text

where  $V_r$  is a reference volume,  $\delta_A$ ,  $\delta_C$  the solubility parameter for structural units A and C, respectively,  $\rho$  is density,  $F_i$  group molar attraction constant and M the molecular weight of the repeat unit. For the copolymer,  $\delta$ was calculated taking into account the ratio of basic units from which it may be assumed to be derived<sup>45</sup>. Calculation of  $\chi_{AC}$  using these concepts is valid since no strong specific forces are involved.

The results of such a calculation are given in *Figure 8*  m terms of the copolymer composition dependence of  $\chi_{12}$ . The  $\chi_{12}$  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  $\chi_{12}$  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  $\chi_{AC}$ , hence of  $\chi_{12}$ , at different temperatures was made by combining equation  $(6)$  with the expression<sup>46</sup>  $\partial \ln \delta / \partial T = -\alpha$ , relating solubility parameter with the coefficient of cubic expansion  $\alpha$ .

Data used in previous calculations are as follows. For the coefficient of thermal expansion, the value of amorphous PET was adopted<sup>47</sup> for PETG;  $\alpha_{\texttt{sPET}} =$  $\alpha_{\text{gPFTG}} = 2.16 \times 10^{-4} \degree \text{C}^{-1}$ . Above  $T_g$  use was made of the Simha–Boyer rule<sup>47</sup>  $(\alpha_1 - \alpha_2)$   $T_g = 0.115$  to obtain  $\alpha_1$ ;  $\alpha_1$ <sub>PET</sub> =  $\alpha_1$ <sub>PETG</sub> = 1.47 × 10<sup>-3</sup> °C<sup>-1</sup>. Calculated solubility parameters at room temperature were  $\delta_{\text{PETamorphous}} = 11.38$  (cal cm<sup>-3</sup>)<sup>172</sup>,  $\delta_{\text{PETused}} = 11.41$  $\frac{(cal\,cm-3)^{1/2}}{PETG} = 10.71 \cdot \frac{(cal\,cm-3)^{1/2}}{PETG}$ . Molar volumes are:  $V_{\text{PET}} = 144 \text{ cm}^3 \text{ g} \text{ mol}^{-1}$  adopted as  $V_r$ ,  $V_{\text{PETG}} = 163 \text{ cm}^3 \text{ g} \text{ mol}^{-1}$ .  $\rho$  (PETG calculated)<sup>48</sup> = 1.383 g cm<sup>-3</sup> at 25<sup>o</sup>C,  $\rho$  (amorphous PET)<sup>47</sup> = 1.330 g cm<sup>-3</sup> and  $\rho$  (crystal PET)<sup>47</sup> = 1.455 g cm<sup>-3</sup> at 25°C. To calculate  $\varphi_2$  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  $\chi_{12}$  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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## **REFERENCES**

- 1 Papadopoulou, C. P. and Kalfoglou, N. K. *Eur. Polym. J.* in press
- 2 De Winter, W., Marien, A., Heirbaut, W. and Verheijen, I. *Makromol. Chem. Macromol. Syrup.* 1992, 57, 253
- 3 La Mantia, F. P. and Vinci, M. *Polym. Degrad. Stabil.* 1994, 45, 121
- 4 Dealy, J. M. and Wissbrun, K. F. in 'Melt Rheology and its Role in Plastics Processing', Van Nostrand-Reinhold, New York, 1990, p. 523
- 5 Stein, R. S., Khambatta, F. B., Warner, F. P., Russel, T., Escala, A. and Balizer, *E. J. Polym. Sci., Polym. Symp.* 1978, 63, 313
- 6 Escala, A. and Stein, R. S. in 'Multiphase Polymers" (Eds S. L. Cooper and G. M. Esters), Adv. Chem. Ser. No. 24, Am. Chem. Soc., 1979, p. 455
- 7 Avramova, N. *Polymer* 1995, 36, 801
- 8 Murff, S. R., Barlow, J. W. and Paul, *D. R. J. Appl. Polym. Sei.*  1984, 29, 3231
- 9 Kim, W. N. and Burns, *C. M. J. Polym. Sci., Polym. Phys. Edn*  1990, 28, 1409
- 10 Kanai, H., Sullivan, V. and Auerbach, *A. J. Appl. Polym. Sci.*  1994, 53, 527
- 11 Yoon, H., Feng, Y., Qui, Y., Han, *C. C. J. Polym. Sci., Polym. Phys. Edn* 1994, 32, 1485
- 12 Montaudo, G., Puglisi, C. and Samperi, F. *Polym. Degrad. Stabil.* 1991, 31,291
- 13 Wang, L.-H., Lu, M., Yang, X. and Porter, *R. S. J. Macromol. Sei., Phys.* 1990, B29, 171
- 14 Robeson, M. J. *Appl. Polym. Sci.* 1985, 30, 4081
- 15 Kim, B. K., Jeong, H. M. and Lee, *Y. H. J. Appl. Polym. Sci.*  1990, 40, 1805
- 16 Cheung, M. F., Garduner, K. R., Golovoy, A. and Van Oene, *H. J. Appl. Polym. Sci.* 1990, 40, 977
- 17 Legros, A., Carreau, P. J. and Favis, B. D. *Polymer* 1994, 35, 758
- 18 Stewart, M. E., Cox, J. A. and Naylor, M. D. *Polymer* 1993, 34, 758
- 19 Zachmann, H. G. and Andresen, E. *Colloid. Polym. Sei.* 1994, 272, 1352
- 20 Guo, M. and Zachmann, H. G. *Polymer* 1993, 34, 2503
- Brown, C. S. and Alder, P. T. in 'Polymer Blends and Alloys' (Eds M. J. Folkes and P. S. Hope), Blackie, London, 1993, chapter 8
- 22 Shin, B. Y., Jang, S. H. and Chung, I. J. *Polym. Eng. Sci.* 1992, 32, 73
- 23 Shin, B. Y. and Chung, I. J. *Polym. Eng. Sei.* 1990, 30, 13
- 24 Lee, W. and Di Benedetto, A. T. *Polymer* 1993, 34, 684
- 25 Nakano, Y., Makino, M., Yamane, H., Kimura, Y. and Kitao, T. *Japan J. Polym. Sei. Teehnol.* 1992, 49, 635
- 26 Perkins, W. G., Marcelli, A. M. and Frerking, H. W. Jr. *J. Appl. Polym. Sei.* 1991, 43, 329
- 27 Utracki, L. A. in 'Polymer Alloys and Blends', Hanser, Munich, 1989, p. 287
- 28 McCrum, N. G., Read, B. E. and Williams, G. in 'Anelastic and Diectric Effects in Polymeric Solids', Wiley, New York, 1967, p. 501
- 29 McCrum, N. G., Read, B. E. and Williams, G. in 'Anelastic Dielectric Effects in Polymeric Solids, Wiley, New York, 1967, p. 503
- 30 Hoffman, J. D. and Weeks, J. *J. J. Res. Natl Bur. Stands.* 1962, 66A
- 31 Kimura, M. and Porter, *R. S. J. Polym. Sci., Polym. Phys. Edn*  1983, 21,367
- 
- 32 Nadkarni, *V. M. J. Appl. Polym. Sci.* 1992, **46**, 339 Olabisi, O., Robeson, L. M. and Shaw, M. T. ir Olabisi, O., Robeson, L. M. and Shaw, M. T. in 'Polymer-Polymer Miscibility', Academic Press, New York, p. 287
- 34 Nishi, T. and Wang, T. T. *Maeromoleeules* 1975, 8, 909
- 35 Wunderlich, B. in 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980, p. 69
- 36 Wunderlich, B. in 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980, p. 63
- 37 Yang, J., Hadjiioannou, G. and Stein, *R. S. J. Polym. Sci., Polym. Phys. Edn* 1982, 21, 159
- 38 Runt, J., Miley, D. M., Gallagher, K. P., Zhana, X., Barron, C. A. and Kumar, S. K. *Polym. Adv. Teehnol.* 1993, 5, 333
- 39 Huo, P. P. and Cebe, P. *Maeromolecules* 1993, 26, 3127
- 40 Gallagher, K. P., Zhang, X., Runt, J. P., Huynh-ba, G. and Lin, J. S. *Macromoleeules* 1993, 26, 588
- 41 Greco, P. and Martuscelli, E. *Polymer* 1989, 30, 1475
- 42 Kwei, T. K. and Frisch, *H. L. Macromolecules* 1978, 11, 1267
- 43 Margaritis, A. G. and Kalfoglou, *N. K. J. Polym. Sci., Polym. Phys. Edn* 1988, 26, 1595
- 44 ten Brinke, G., Karasz and MacKnight, W. J. *Macromolecules*  1983, 16, 1827
- 45 Krause, S. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vol. 1, Academic Press, New York, 1978, chapter 2
- 46 Sanchez, I. C. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Vol. 1, Academic Press, New York, 1978, chapter 3
- 47 Krevelen, D. W. 'Properties of Polymers', Elsevier, New York, 1972, chapter 4
- 48 Askadskii, A. *Pure Appl. Chem.* 1976, 46, 19