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A free volume approach to the mechanical behaviour of miscible polycarbonate blends

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Abstract. Composition-dependent mechanical properties and free volumes are compared for miscible, amorphous blends of bisphenol-A polycarbonate (PC) with (a) polyaryloxysiloxane (PAS), (b) a copolyester of 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids (EASTAR) and (c) an experimental polyester of 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexanedimethanol (CDACD). The free volumes were measured by the positron annihilation lifetime spectroscopy (PALS) technique. The strength of specific interactions, as indicated by T_g data, is relatively weak in all of the blends. However, the fractional free volume quantity measured by PALS ($\tau_2^3 I_3$) is less than additive in the polyester blends and is additive, or greater than additive, in the PC–PAS blends. The mechanical behaviour of the blends can be rationalized in terms of the free volume behaviour. The polyester blends which lose free volume (contract) on mixing exhibit higher than averaged yield strengths and brittle impact responses. The PC–PAS blends which retain or gain free volume on mixing exhibit averaged yield strengths and averaged ductile impact responses of the constituent polymers.

1. Introduction

The mechanical behaviour of glassy polymers (and glassy miscible polymer blends) can be described in terms of a competition between yielding and crazing [1–3]. Yield can be understood in terms of the slipping of chains past each other in some activation volume which is the product of a molecular dimension and the area swept out as a chain segment jumps in the direction of stress [4]. The activation volume is a non-physical parameter derived from the activated rate process theory of the flow of solids [4]; however, it has been suggested that the calculated activation volume should be related to the polymeric free volume (the space between and along polymer chains) [5, 6]. Bultel *et al* [7] have described the free volume as point defects which influence the jump frequency of molecular units and hence the flow of the solid at yield. The ability of a polymer to deform and dissipate energy under impact also depends on the ease with which the chains can slide past each other or change conformations via in-chain rotations [2]. Hence chain mobility influences the yield and impact behaviour of glassy polymers. Attempts to correlate molecular structure and the available free volume with chain mobility and mechanical properties have led to the general

belief that any process which reduces free volume reduces chain mobility, increases yield strength and reduces impact strength [2].

There exists a strong theoretical base relating the mechanical behaviour of amorphous polymers to the free volume available for chain slippage and chain mobility [2, 8–12]. This free volume is conceptually constituted by spaces between and along the chains having dimensions of the order 2–10 Å. However, quantitative methods for calculating the free volume from indirect measurements, such as density, restrict the free volume to the static or interstitial unoccupied spaces that result from less than perfect chain packing [13, 14]. A dynamic or fluctuating free volume, which is evident from small-angle x-ray scattering (SAXS) and xenon nuclear magnetic resonance (NMR) measurements, is also present in glassy polymers. Sub- T_g segmental mobility, which plays an important role in transport [15] and mechanical [8] properties, is a manifestation of such a fluctuating free volume.

Numerous authors conjecture that both the static and the dynamic free volume play important roles in chain mobility and hence mechanical behaviour [8, 16, 17]. Positron annihilation lifetime spectroscopy (PALS) provides a direct probe of a particular fraction of the static and dynamic polymeric free volume. An injected positron binds with an electron of parallel spin to form ortho-positronium (oPs). According to the theory of Brandt *et al* [18] the oPs annihilates by pick-off with an annihilation rate, λ_3 , which is a function of the free volume cavity size. Ortho-positronium pick-off annihilation is a quenching process during which the positron in oPs (localized in free volume cavities) annihilates with an electron, of opposite spin, from the surrounding cavity wall. The oPs pick-off lifetime, τ_3 ($\tau_3 = 1/\lambda_3$), reflects the mean free volume cavity radius. The relative number of oPs pick-off annihilations, I_3 , reflects the oPs formation probability and the number of free volume sites in the volume of the polymer probed. Brandt *et al* [18] and subsequent authors [19, 20] give the typical range of radii of free volume cavities probed by the oPs as approximately 2–6 Å. This size range corresponds to inter- and intra-molecular distances in polymers and the root mean square end-to-end distances of average polymer repeat units (2–10 Å) [21].

Models have been proposed for calculating free volume parameters from the PALS data, such as the average spherical hole volume, V_f (with units of Å³), or fractional free volume, f (with percentage units) [22, 23]. PALS can measure a particular fraction of the polymeric free volume: the fraction probed by oPs. For the present work the PALS parameter τ_3 (ns) will be discussed as a measure of the relative average free volume cavity radius, τ_3^3 (ns³) as a relative spherical cavity size, I_3 (%) as a relative concentration of free volume and $\tau_3^3 I_3$ (ns³%) as a relative fractional free volume. These PALS parameters do not have the units of a physical volume because they are based on the raw PALS data without the use of empirical parameters or constants derived from thermal expansion measurements and the WLF reference free volume [22]. This nomenclature based on the PALS parameters reminds the reader that the free volume measured by PALS represents only that fraction of the total free volume that is probed by the oPs.

Previous work has shown that the PALS free volume can be correlated with physical, mechanical and transport properties of amorphous and semi-crystalline polymers [19, 22–26]. Recently, PALS studies of polymer blends have been performed by several research groups, in the miscible systems PC–THERMX [27], PC–PAr [28], PMMA–PEO [29], PHBA–PHNA [30], PMMA–PVF [29], PC–PCL [31], PPO–PS [32], TMPC–PS [33]; in the partially miscible blend systems PC–PBT [34], PC–PMMA [35], PC–Nylon [31, 32] and Vectra–PEI [36]; and in the immiscible systems Nylon–PP [31, 32], PP–LDPE [37], Vectra–PP [38] and PS–PC [33]. The nomenclature for these polymers follows: PC is bisphenol-A polycarbonate, PAr is polyarylate, PMMA is polymethylmethacrylate, PEO is polyethyleneoxide, PHBA is the polyester of hydroxybenzoic acid, PHNA is the polyester

of hydroxynaphthoic acid, PVF is polyvinylidene fluoride, PCL is polycaprolactone, PPO is poly(2,6-dimethyl-1,4-phenyleneoxide), PS is polystyrene, TMPC is tetramethyl bisphenol-A polycarbonate, PBT is poly(butylene terephthalate), PEI is polyetherimide, PP is polypropylene and LDPE is low-density polyethylene. Immiscible blends, in general, possess a phase-separated morphology with weak interfaces and inferior mechanical properties [39]. Use of compatibilizers to knit the interfaces and improve mechanical properties has been studied by PALS, showing that the I_3 parameter was sensitive to the improved packing and bonding at the interfaces [37]. The mechanical properties of glassy partially miscible polymer blends are usually additive or inferior [39]. In partially miscible blends, approximate linear additivity on a weight percentage basis has been observed in the τ_3 and I_3 components with composition. In partially miscible amorphous polymer blends the volume fraction of regions containing a mixture of segments is normally a very small fraction of the blend. PALS sampling of partially miscible blends then consists principally of averaging the free volumes of the essentially pure constituent polymers in their gross blend concentrations. An additivity of the free volumes of the constituent polymers is therefore observed [35]. In miscible polymer blends, less than additive behaviour of τ_3 over the composition range was first observed by Mayo and co-workers [31, 32] and interpreted as a contraction of free volume on blending in accord with the predictions of mean field thermodynamic theory for blends. Subsequent studies have confirmed these trends in miscible amorphous blends [28, 29, 33] or semicrystalline blends of low percentage crystallinity [27]. This negative deviation from linearity has been discussed in terms of specific interactions and packing considerations [28, 33]. In contrast to glassy partially miscible blends, the mechanical properties (yield strengths) of glassy miscible blends are usually superior [39].

As mentioned above, the PALS parameter I_3 represents a relative measure of the concentration of free volume cavities in the volume probed. As crystallinity increases (as the amount of ordered material in the volume probed increases) the relative number of free volume sites in the volume probed (I_3) decreases [22, 40, 41]. In general, the mean radius of the free volume cavities, represented by τ_3 , remains unchanged with variation in the degree of crystallinity [22, 40, 41]. Equations have been developed to correct the PALS parameters for the effect of crystallinity in constituent polymers [40, 41] and miscible blends [40] to permit examination of the amorphous region free volume characteristics. The method of correction in miscible blends does not account for the constraint on the amorphous miscible regions caused by the crystalline regions [27, 40]. Hence the effects of such constraints can be probed by PALS [27]. In addition, a correction for the effect of crystallinity on composition can be made and amorphous properties, such as T_g or PALS free volume, can be presented as functions of the amorphous composition rather than as functions of total blend composition [27, 40].

Zipper [43] has shown that, for miscible polyester blends of very low percentage crystallinity (<4%), the correction to I_3 results in changes that fall within the population standard deviation of the data. For example, in the copolyester THERMX PCTA6761 (a copolyester of cyclohexanedimethanol and terephthalic and isophthalic acids, hereafter referred to as THERMX) a change in crystallinity of 3% causes a change in the I_3 parameter of 0.2% absolute (the population standard deviation of the component is $\pm 0.3\%$ absolute) [43]. A comparison of the fractional free volume parameter $\tau_3^3 I_3$ for miscible PC-THERMX blends of low percentage crystallinity (percentage crystallinity of the blend, $X < 7\%$) and higher percentage crystallinity ($15\% < X < 30\%$) is shown in figure 1. In blends of low crystallinity, it has been shown [43] that the negative deviation from linearity of $\tau_3^3 I_3$, as a function of blend composition, corresponds to a greater than additive yield strength and

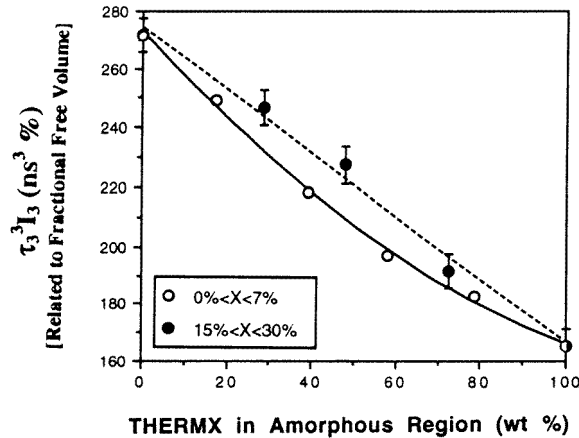


Figure 1. The composition-dependence of the PALS parameter $\tau_3^3 I_3$, (related to fractional free volume) in PC-THERMX blends of low and higher percentage crystallinity. Broken lines represent linear additivity with weight percentage composition. The full line is drawn to indicate the actual trend. Percentage crystallinity of THERMX between 0 and 7% of the blend (○); percentage crystallinity of THERMX between 15 and 30% of the blend (●).

a less than additive elongation in response to breakage and impact energy. However, as shown in figure 1, in miscible polyester blends of higher crystallinity ($15\% < X < 30\%$), the fractional free volume parameter $\tau_3^3 I_3$ is approximately additive with blend composition (corrected for crystallinity) and this change in the fractional free volume behaviour has been attributed to the constraint imposed by the crystals which causes a dilation of the amorphous free volume [27]. Support for this postulate comes from the recent work of Marand *et al* [44] who predict that the amorphous density must decrease with increased crystallinity based on the discrepancies between density and DSC crystallinities in semicrystalline polymers. An important conclusion drawn from the data of figure 1 is that miscible blends of semicrystalline polymers may or may not show less than additive free volume in the amorphous regions as a function of composition. In other words, such blends can be miscible without a contraction of free volume in the amorphous miscible region; however, the additive PALS free volume parameters of these miscible blends are most probably caused by a constraint from the crystalline phase [27, 29]. Because of the effect of crystallinity on mechanical properties, no conclusion regarding the relationship between the free volume and the mechanical behaviour of the PC-THERMX blends with higher degrees of crystallinity (with additive amorphous free volume) can be made.

Based on the work to date, it is of interest to compare the mechanical behaviour of glassy miscible blends that display additive free volume with those that display less than additive free volume with composition. The present study addresses the behaviour of the PALS free volume parameters in three miscible blend systems with the common component of PC. These blends are the PC-polyaryloxysiloxane (PAS) system, the PC-EASTAR system and the PC-CDACD system (EASTAR and CDACD are defined in the following section). The blends here described are amorphous or of such low crystallinity that effects of crystallinity on the free volumes and physical properties of the blends are negligible. The effects of composition and hence of polymer structure and interactions on the free volume and mechanical behaviour of these miscible blends are compared and contrasted.

2. Experimental

2.1. Materials

Two bisphenol-A polycarbonates (PC) were used. These were Lexan 141 resin (General Electric Company) and Makrolon 2608 resin (Mobay). EASTAR A150 resin (Eastman Chemical Company) is a low-crystallinity ($T_g = 84^\circ\text{C}$ and $T_m = 269^\circ\text{C}$) copolyester of 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids. CDACD (Eastman Chemical Company) is a low-crystallinity ($T_g = 65^\circ\text{C}$ and $T_m = 212^\circ\text{C}$) experimental polyester of 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexanedimethanol. Polyaryloxysiloxane (PAS) is an aryloxy-dimethylsiloxane polymer invented and developed at General Electric Corporate R&D [45]. This normally amorphous polymer has a T_g of 141°C and can be crystallized with some difficulty to give a semicrystalline polymer with T_m of 271°C . Representations of the chain unit structures of PAS and the other polymers used in this study are shown in figure 2.

The following blends were prepared and studied.

(i) PC-PAS. The blend was prepared by co-extrusion of Lexan 141 resin and PAS at the General Electric Corporate R&D Center in Schenectady, NY. The PC and PAS were vacuum dried at 135°C for 4 h prior to melt blending in a 20 mm co-rotating twin-screw extruder. Melt temperatures at the die were in the range $288\text{--}294^\circ\text{C}$ depending on composition. After drying, the extruded pellets were injection moulded using a 28 tonne moulding machine with a nozzle set-point of 257°C [46].

(ii) PC-EASTAR. Lexan 141 and EASTAR A150 resin were vacuum dried at 135°C for 4 h, melt-blended and co-extruded (melt temperatures $280\text{--}300^\circ\text{C}$ depending on composition [47]) using a 1.25 inch single screw extruder in Melbourne, Australia. It should be noted that EASTAR was previously known as Kodar. The blends were subsequently dried and injection-moulded on an 80 tonne Mieke moulder. A transesterification inhibitor was added to the extrusion mixture. Fourier transform infrared spectrometry and solubility tests indicated that negligible transesterification had occurred in the blends.

(iii) PC-CDACD. Makrolon 2608 resin and CDACD were melt-blended by compounding on a 28 mm Werner & Pfleiderer twin-screw extruder and subsequently injection-moulded on a Boy 22S injection-moulder. An extrusion temperature of 280°C was used and a transesterification inhibitor was added. Nuclear magnetic resonance measurements on the blends indicated that negligible transesterification had occurred. The blending and moulding operations were performed at Eastman Chemical Company in Kingsport, TN.

2.2. Characterization

Differential scanning calorimetry (DSC) was used to confirm a single, composition-dependent glass transition temperature, T_g , in all blends in addition to determining the approximate amount of crystallinity present. The PC-EASTAR system was analysed using a Perkin Elmer DSC7 at $10^\circ\text{C min}^{-1}$; the PC-CDACD system was analysed using a Du Pont Model 912 at $20^\circ\text{C min}^{-1}$ and the PC-PAS system was analysed using a Perkin Elmer DSC2C at $20^\circ\text{C min}^{-1}$. The T_g values are reported as the temperature by which one-half of the specific heat increase in the glass transition region had occurred. The values for the PC-PAS system are for samples heated above T_m and quenched (that is, subjected to a second heat run), whereas the PC-EASTAR and PC-CDACD samples were measured in the as-moulded state (first heat run). Uncertainties in the reported T_g (DSC) are estimated

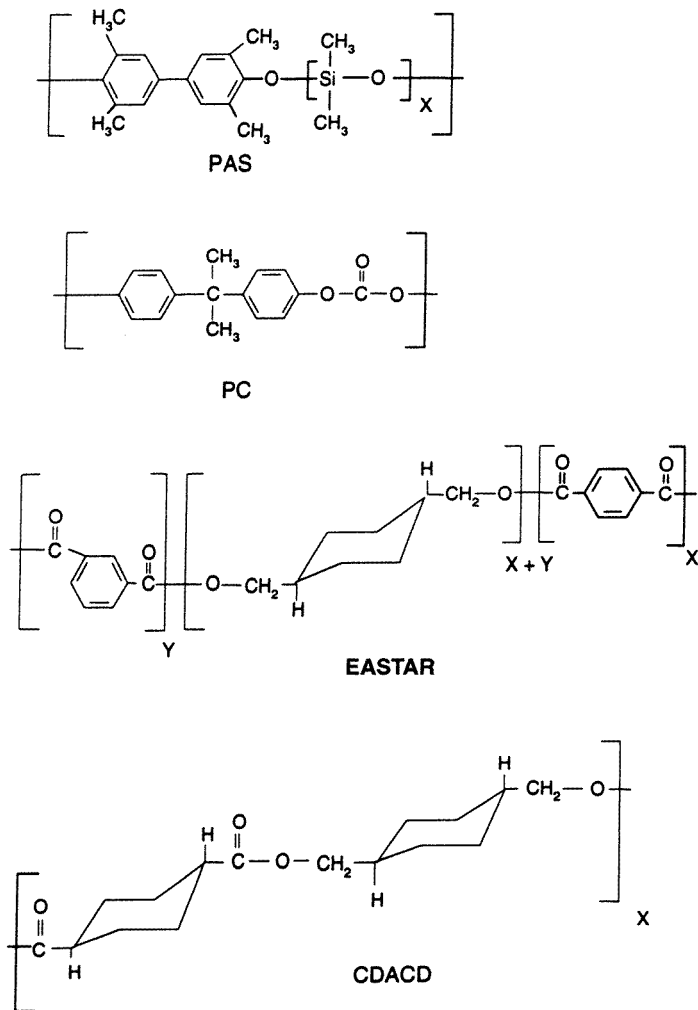


Figure 2. Unit structures of the polymers: bisphenol-A polycarbonate (PC), a copolymer of 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids (EASTAR), an experimental polyester of 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexanedimethanol (CDACD) and polyaryloxysiloxane (PAS).

to be 1 °C for the PC–polyester blends and 0.5 °C for the PC–PAS blends. The heats of fusion of EASTAR, CDACD and PAS crystals were not determined. For EASTAR and CDACD, a heat of fusion of 124.7 J g⁻¹, which is the heat of fusion of THERMX [43, 48], was used as an estimate. This should result in a high estimate of the degrees of crystallinity for EASTAR and CDACD. A heat of fusion of 138 J g⁻¹ was estimated for PAS based on the group contribution theory of van Krevelen [21]. Dynamic mechanical analysis (DMA) was used to measure $T_g(\text{DMA})$ as the temperature corresponding to the $\tan \delta$ loss peak. An uncertainty of 1 °C is estimated for the $T_g(\text{DMA})$ values. Samples were measured at a fixed 1 Hz frequency and at 2 °C min⁻¹ heating rate. Tensile yield strength was measured at 23 °C according to ASTM standard D638. Notched Izod impact strength

was measured at 23 °C according to ASTM standard D256. Density was measured using the Archimedeian method in distilled water at room temperature. A possible uncertainty of 0.009 g cm⁻³ exists in the density values. The positron annihilation lifetime spectroscopy (PALS) apparatus was temperature-stabilized at 22 °C and consisted of an automated EG&G Ortec fast-fast coincidence system with a ²²Na resolution of 250 ps. The 1.3 MBq ²²NaCl source was a 2 mm spot source sandwiched between two Ti foils (2.54 μm foils). The source gave a one-component best fit to 99.99% pure, annealed, chemically polished aluminium ($\tau = 166$ ps); hence, no source correction was used in the analysis of the data with the PFPOFIT program [49]. The para-positronium component was fixed at $\tau_1 = 125$ ps. Each spectrum contained 30 000 peak counts (approximately a million integrated counts), and five spectra were collected for each sample; results are the mean of the five spectra, standard deviations are population standard deviations for the five spectra. The spectra could be best modelled as the sum of three decaying exponentials; only the third component (τ_3 , I_3) showed systematic variation with composition and will be reported. The PALS results did not vary as a function of contact time with the ²²Na source. All samples were studied after several months of ambient temperature/humidity storage such that a 'quasi-equilibrium' as-moulded state at room temperature had been attained.

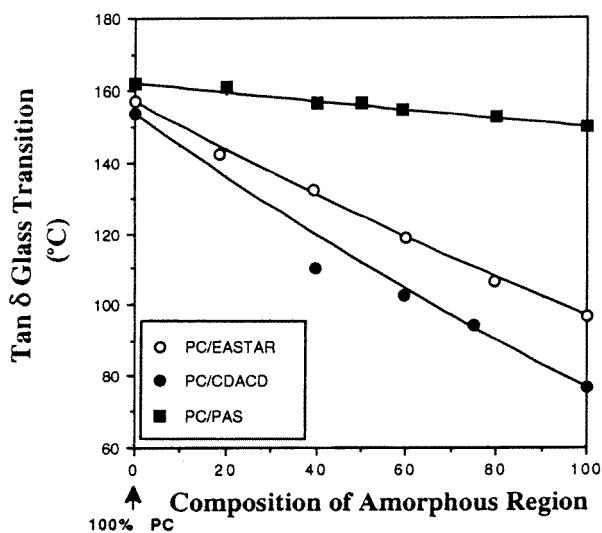
3. Results and discussion

The percentage crystallinity, density and PALS free volume parameters (τ_3 and I_3) for the four polymers and three binary blend systems are presented in table 1. T_g (DSC), T_g (DMA), tensile yield strength and notched Izod impact data are presented in table 2. Only the non-blended polyesters and the PAS are noted to contain any significant, although low, degrees of crystallinity. All the blends and the PC are found to be completely amorphous or to have less than 2% crystallinity. The contribution of these very small crystal contents to the particular physical properties here examined is negligible. The PC does not crystallize in these blends, given their thermal history, and it is assumed for the purpose of calculation that the crystalline phase is pure polyester (EASTAR or CDACD) or PAS. Table 1 shows the negligible effect of crystallinity on the composition of the amorphous region. Although the effect of crystallinity in these systems is minimal, the composition of the amorphous region is utilized to discuss amorphous properties such as the glass transition and the PALS free volume [27].

Figure 3 displays the T_g (DMA) behaviour as a function of blend composition. The DMA data are used because first-run data were available for all of the systems. (The DSC data for the PC-PAS system presented in table 1 were measured during the second heat run following quenching from above the melting point of PAS). The presence of a single, composition-dependent T_g in the blends is used to classify the blends as miscible [50]. It has been suggested that DMA data are useful for blends of polymers having a minimum T_g difference of 20 °C. Jordan and Shultz [46] have presented further evidence for miscibility in the PC-PAS blends based on TEM, NMR and crystallization studies. The full width at half maximum (FWHM) of the $\tan \delta$ loss peak can be used to give an indication of blend homogeneity, with broader peaks indicative of a wider range of mobility environments. The values of FWHM of the $\tan \delta$ loss peaks for the PC-PAS and PC-EASTAR blends were identical to that of the broadest constituent polymer whereas the values of FWHM for the PC-CDACD blends were 10–30% broader than that of the broadest constituent polymer. It should be remarked that a plot of the T_g (DSC) versus the weight fraction of PC for the PC-PAS blends was found to have a somewhat sigmoidal shape [46]. These T_g (DSC) data were the only indication that this system might not be completely homogeneous on the

Table 1. Composition, percentage, crystallinity, density and PALS free volume parameters for the PC–polyester and PC–PAS blends.

Composition (wt.%) of polyester of PAS	Degree of crystallinity of the blend ($\pm 1\%$)	Composition of the amorphous region (wt.%)	τ_3 (± 0.03 ns) related to free volume cavity radius	I_1 ($\pm 0.3\%$) related to free volume concentration	Density (± 0.009 g cm $^{-3}$)
0% EASTAR	0	0	2.043	31.993	1.202
20% EASTAR	1.6	18.7	1.962	32.172	1.204
40% EASTAR	0.9	39.5	1.897	31.153	1.202
60% EASTAR	0.5	59.8	1.843	30.198	1.200
80% EASTAR	1.5	79.7	1.810	28.711	1.200
100% EASTAR	5.9	100	1.775	27.365	1.198
0% CDACD	0	0	2.029	31.970	1.200
40% CDACD	0.2	39.9	1.873	27.780	1.178
60% CDACD	0.9	59.3	1.830	27.240	1.165
75% CDACD	0	75	1.832	26.630	1.158
100% CDACD	4.0	100	1.842	29.720	1.140
0% PAS	0	0	2.008	31.349	1.200
20% PAS	0	20	2.059	32.616	
40% PAS	0	40	2.072	33.869	
50% PAS	0	50	2.076	34.553	
60% PAS	0.8	59.7	2.099	35.350	
80% PAS	0	80	2.129	36.526	
100% PAS	3.0	100	2.121	37.575	

**Figure 3.** Composition dependence of the glass transition temperatures as measured by DMA. The full lines represent the Fox equation [52]: PC–EASTAR blends (\circ), PC–CDACD blends (\bullet) and PC–PAS blends (\blacksquare).

segmental scale.

The T_g (DMA) data show reasonable agreement with the Fox [51] equation (displayed

Table 2. Composition, glass transition temperatures, tensile yield strength and impact strength of the PC–polyester and PC–PAS blends.

Composition (wt.%) of polyester of PAS	T_g (DSC) ($\pm 1^\circ\text{C}$)	T_g (DMA) ($\pm 1^\circ\text{C}$)	Tensile yield strength (MPa)	Notched Izod impact strength (J m^{-1})
0% EASTAR	148.0	157.3	59.5	946
20% EASTAR	131.5	142.4	59.4	122
40% EASTAR	118.6	132.2	56.6	98
60% EASTAR	105.4	118.7	53.8	89
80% EASTAR	93.7	106.5	50.4	94
100% EASTAR	83.8	96.8	46.9	2012
0% CDACD	148.0	154.0	72.7	913
40% CDACD	110.0	110.0	66.1	75
60% CDACD	94.5	102.5	57.9	48
75% CDACD	81.7	94.0	52.1	27
100% CDACD	67.4	77.0	44.6	662
0% PAS	149.1	162	75.2	945
20% PAS	148.6	161	72.7	795
40% PAS	146.3	157	69.4	731
50% PAS	144.7	157	67.8	678
60% PAS	142.6	155	65.3	662
80% PAS	Not measured	153	62.8	651
100% PAS	139.8	150	59.5	668

as full lines in figure 3). The Fox equation is semi-empirical and is based on the assumption of volume additivity [52]. The Flory–Huggins [53] interaction parameter, χ , related to the strength of the specific interactions between the components of the blends, can be derived from the T_g data [54]. Blends with very strong specific interactions show higher T_g values than do those represented by a straight-line, weight-fraction-averaged T_g . Blends with very weak or relatively weak specific interactions show a negative deviation from linear additivity. The polyester blends (PC–EASTAR and PC–CDACD) show a negative deviation from linear additivity. The PC–PAS blends exhibit a T_g (DMA) versus weight percentage PAS plot which is approximately linear; however, due to the narrow range of 12°C between the T_g (DMA) values for PC and PAS a definitive statement of linearity cannot be made. It is concluded from the T_g (DMA) data presented in figure 3, that the blends in the present study are miscible, with relatively weak favourable specific interactions between the components.

Specific volumes for the PC–polyester systems are shown in figure 4. Density data for the PC–PAS system were not measured. Miscible blends often show less than additive specific volumes. This deviation is attributed to the enthalpically favourable (exothermic) interactions which cause a decrease in free volume on mixing [55–57]. The specific volume additivities indicated in figure 4 suggest that the specific interactions in these blends are relatively weak and that negative deviation from weight fraction additivity of the specific volumes of the individual polymer components has not been proven.

The PALS data are presented as raw τ_3 and I_3 values in figures 5 and 6. The data are not corrected for crystallinity [40], but the composition is corrected, hence the data are plotted as functions of amorphous composition. Simon *et al* [40] and Zipper *et al* [27] have shown that, for miscible polyester blends of low crystallinity (<4%), the correction results

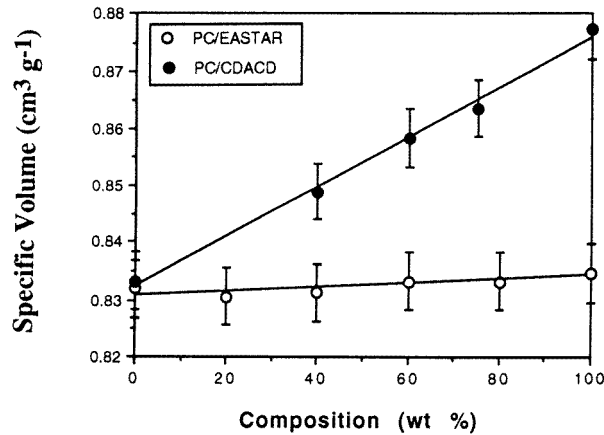


Figure 4. The composition-dependence of the specific volume. The best linear least squares fits are shown: PC–EASTAR blends (○) and PC–CDACD blends (●).

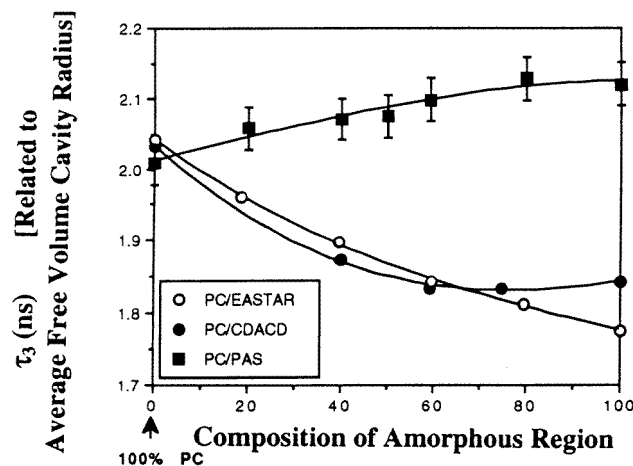


Figure 5. The composition-dependence of the oPs pick-off lifetime τ_3 (related to the average free volume cavity radius). Curves are drawn to indicate trends: PC–EASTAR blends (○), PC–CDACD blends (●) and PC–PAS blends (■).

in changes within the population standard deviation of the PALS data. Simon *et al* [40] have discussed in detail the implications of this type of correction in miscible blends. The effect of polymer structure on the local electron density and free volume is reflected in the PALS data. The parameter τ_3 gives an indication of the electron density in the vicinity of the oPs. The oPs localizes in the space between and along chains and at chain ends (free volume cavities), and the lifetime gives an indication of the average radii of these cavities. The parameter I_3 gives an indication of the oPs formation probability and the relative number of free volume cavities in the volume of polymer probed. This volume probed is typically 1 mm^3 . The polyester blends (PC–EASTAR and PC–CDACD) show fewer and smaller free volume cavities with increasing polyester content whereas the PC–PAS blends show an

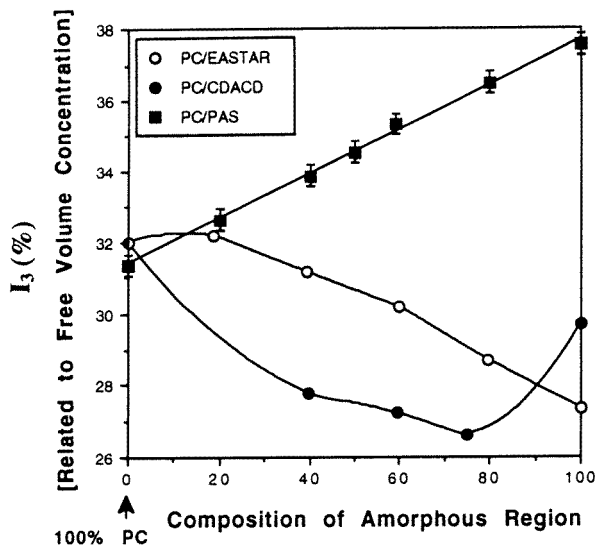


Figure 6. The composition-dependence of the oPs pick-off intensity I_3 (related to the average free volume cavity radius). Curves are drawn to indicate trends: PC-EASTAR blends (\circ), PC-CDACD blends (\bullet) and PC-PAS blends (\blacksquare).

increase in the relative size and number of free volume cavities with increasing PAS content. A comparison of the PALS free volume data and the density data indicates that the PALS measure of free volume is not directly coupled to the free volume measured by density. This difference may be attributed to three main factors. First, the free volume measured by PALS is that fraction of the total free volume that can be probed by oPs, and that fraction is dependent on the size of the oPs probe and the size of the free volume cavities (thus there are lower and upper size limits on the cavities probed). Second, the PALS technique is capable of measuring dynamic (frequency $< 10^9$ Hz) as well as static (interstitial, packing-related) free volume. Third, the PALS technique measures sub-microscopic free volume cavities and thus differs experimentally from the bulk nature of the Archimedean density measurement which includes macroscopic pores in the large specimens used for the measurement and is subject to surface tension effects.

The parameter $\tau_3^3 I_3$ gives an indication of the relative fraction of free volume in the amorphous miscible regions. In the amorphous blends, this fractional free volume should influence mechanical behaviour as a perturbation on the structure [58]. In other words, the constituent polymer structures, entanglement density, thermal history and free volume would result in some value of yield strength or impact energy. The miscible blends would be expected to have mechanical properties intermediate to those of the constituent polymers; however, less than additive fractional free volume could lead to greater than additive yield strength and less than additive impact strength. The effect of free volume on the mechanical properties of polymers has been discussed by Boyer [8] and others [9–12]. The basic premise of free volume-related mechanical properties is that the space between and along chains allows chain slippage, leading to yield and chain mobility contributing to the dissipation of impact energy. If that space between and along the chains (the free volume) is reduced (for example, due to specific interactions on blending or physical ageing, both of which can reduce dynamic free volume by hindering sub- T_g mobility and reduce static free volume

by promoting chain packing) then the flow process is hindered and supplementary stress is needed to allow flow. The yield strength is expected to increase, possibly above the value of the fracture strength, thereby resulting in brittle fracture. Similar yield behaviour has been shown by Bauwens [10] at temperatures below -50°C in glassy polycarbonate, due presumably to the reduced chain mobility and free volume at low temperatures. Hence, because the deformation process corresponds to the cooperative utilization of a number of free volume sites [5], it seems reasonable to correlate the PALS free volume ($\tau_3^3 I_3$) with yield strength and impact energy because both deformation processes involve chain slip and conformation changes.

The PALS free volume parameter $\tau_3^3 I_3$ as a function of composition is shown in figures 7(a)–(c). The polyester blends (PC–EASTAR and PC–CDACD) display less than additive fractional free volume whereas the PC–PAS blends display additive, or possibly greater than additive, fractional free volume as a function of composition. The tensile yield strength of the blend systems is presented in figures 8(a)–(c). The polyester blends (PC–EASTAR and PC–CDACD) exhibit a positive deviation from linear additivity (figures 8(a) and 8(b)). This type of yield behaviour has been observed in many miscible blend systems [56, 57, 59] and has been discussed in terms of the interactions between the blend components which lead to greater than additive molecular packing (less than additive free volume) [59]. The PC–PAS system displays additive yield behaviour (figure 8(c)) which correlates with the additive fractional free volume (figure 7(c)). The impact behaviour is presented in figure 9. The polyester blends are brittle (impact energy $<150\text{ J m}^{-1}$) even though the polyesters and the PC are ductile with high impact energies. The impact energy of the EASTAR polyester, 2012 J m^{-1} [28], is not shown in figure 9. The PC–PAS impact behaviour is approximately additive with composition.

Comparing the PALS free volume parameter $\tau_3^3 I_3$ and mechanical behaviour in the miscible blend systems of the present study shows that a negative deviation from linearity of the relative fractional free volume correlates with a positive deviation from linearity of yield strength and a less than additive response for impact energy. The additive response of the relative fractional free volume in the PC–PAS system correlates with additive yield and impact. Although all three of the blends studied have the favourable segmental interactions necessary for miscibility, it appears that the PC–PAS system has structural aspects which allow miscibility without greater than average packing and without limiting the population of ductile conformations in the blends. The exact nature of the structural differences in these blend systems that contribute to the free volume and mechanical property behaviours has not been determined. The results suggest that favourable specific interactions do not dictate a contraction of free volume in all amorphous miscible blends. In addition, the ability to probe both static and dynamic free volume appears to give the PALS technique sensitivity to the effect on free volume of structural aspects of these blend systems that is not available from specific volume measurements.

4. Conclusions

A contraction of free volume in miscible, amorphous polymer blends may or may not occur. The PC–polyester blends of the present study exhibit the expected [60] less than additive relative free volume fractions (contraction) of miscible polymer blends. This free volume behaviour correlates with a positive deviation from averaged yield strengths and markedly lower impact energies. Additivity of the relative fractional free volumes in the PC–PAS blends correlates with averaged yield and impact strengths. The T_g data indicated that the blend systems studied were miscible with relatively weak specific interactions between

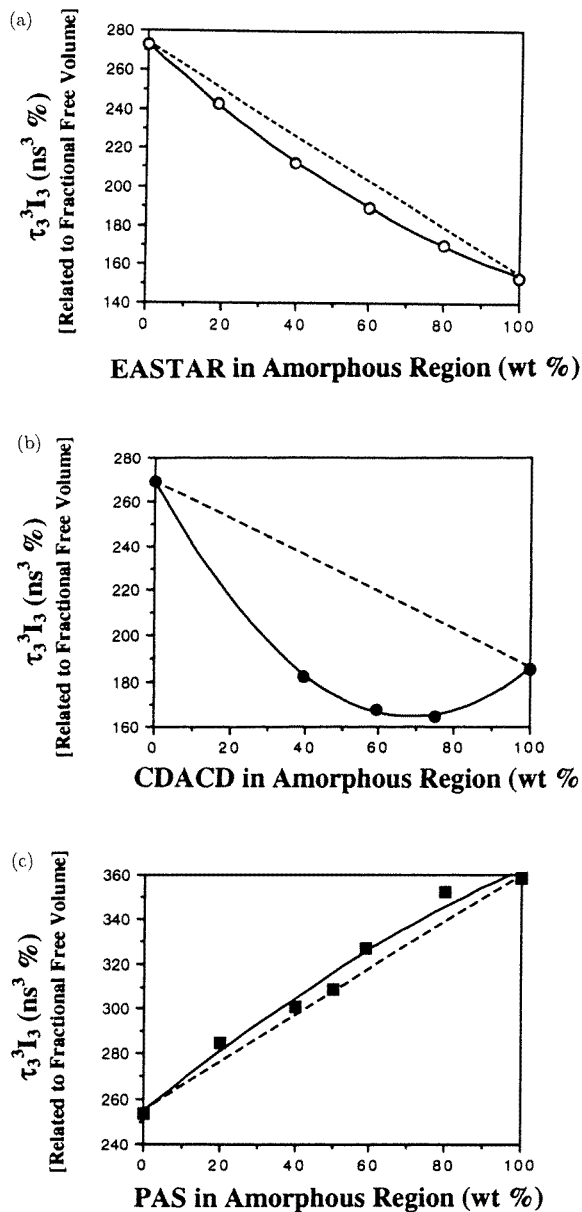


Figure 7. The composition-dependence of the PALS parameter $\tau_3^3 I_3$, (related to the fractional free volume). (a) PC-EASTAR blends (○), (b) PC-CDACD blends (●) and (c) PC-PAS blends (■). Broken lines represent linear additivity with weight percentage composition. Full lines are drawn to indicate actual trends.

the component macromolecules, hence structural aspects of the constituent polymers are suggested as the cause of the variation in behaviour. Specifically it was suggested that the PC-PAS system could blend miscibly without decreasing static free volume through greater than average packing and without decreasing dynamic free volume by limiting the

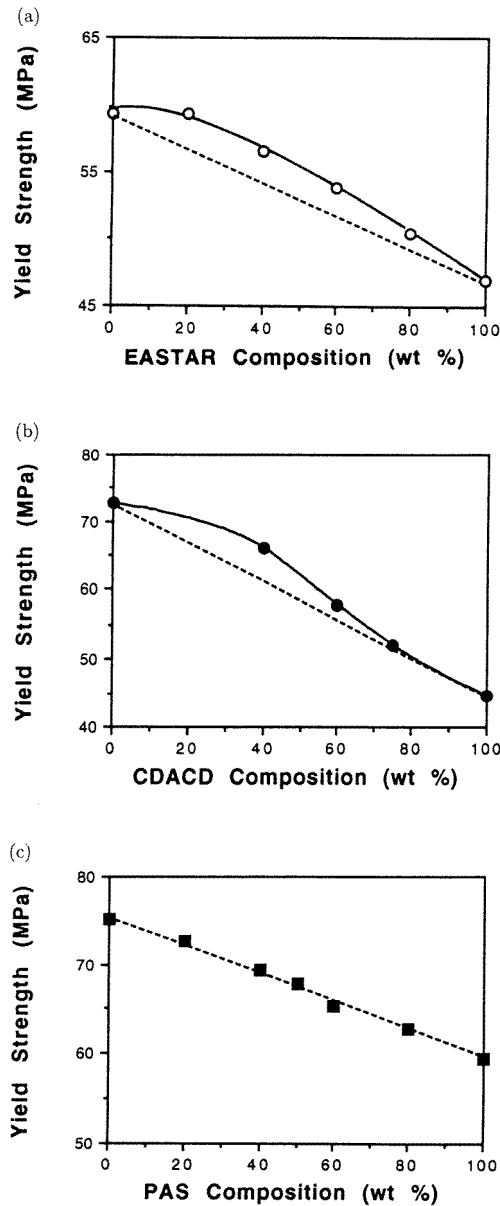


Figure 8. The composition-dependence of the yield strength. (a) PC-EASTAR blends (○), (b) PC-CDACD blends (●) and (c) PC-PAS blends (■). Broken lines represent linear additivity with weight percentage composition. Full lines are drawn to indicate actual trends.

population of ductile conformations in the blends. The direct observation by PALS of less than additive as well as additive free volume behaviours in these miscible polymer blends and the conclusions drawn thus far concur with the work of Wu [61], who suggested that the free volume behaviour (as calculated from viscosity data using WLF parameters) of miscible polymer blends may be additive, less than or greater than additive and is influenced more

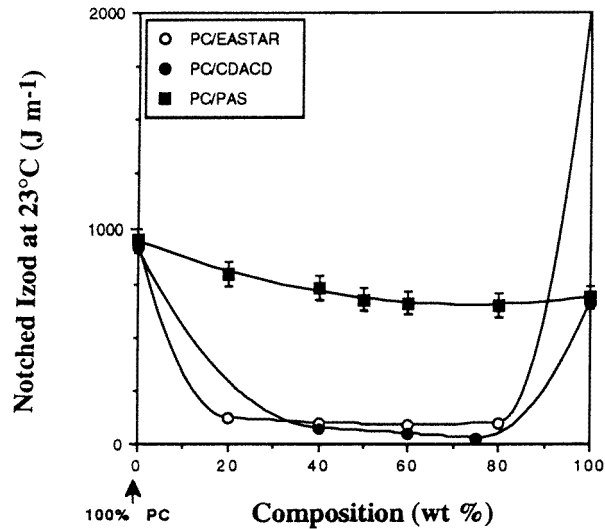


Figure 9. The composition-dependence of the notched Izod impact strength. Full lines are drawn to indicate actual trends: PC–EASTAR blends (○), PC–CDACD blends (●) and PC–PAS blends (■).

by segmental conformation and packing than it is by specific interactions.

The results of the present study were discussed in terms of the concepts of yield and impact behaviour involving the slipping of chains past each other and the changes in chain conformation allowed by the space between and along the chains (the free volume) [2,4]. If the blending results in a less than additive free volume in the blends, then it is possible that the reduced free volume causes reduced molecular mobility and hence prevents chain slippage and dissipation of energy through in-chain rotations or other conformational changes. In the case of additive free volume on blending, the chain mobility and mechanical behaviour would be expected to be additive. The objective of this research programme is to relate the observed free volume behaviour and the molecular structure of the polymers with their mechanical behaviour. Work in progress [58] addresses the modelling of structure and molecular packing in order to predict the activation volume necessary for the segmental mobility of importance to mechanical properties. The present work suggests that the PALS fractional free volume parameter $\tau_3^3 I_3$ is sensitive to that fraction of free volume which affects both low-strain-rate (yield) and high-strain-rate (impact) behaviour in the blend systems.

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