

# Characterization of Thermotropic Liquid Crystalline Polyester/Polycarbonate Blends: Miscibility, Rheology, and Free Volume Behavior

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**ABSTRACT:** Miscibility, rheology, and free volume properties of blends of thermotropic liquid crystalline polymers (TLCPs) (Vectra A950) and polycarbonate (PC) are studied in this work. Despite the unusual increase in  $T_g$  of the PC phase, the blends are found to be generally immiscible. Transesterification may occur during blending and be the cause of the increase of  $T_g$  of the PC phase and the partial miscibility of the blends at high TLCP concentrations. With regard to the melt rheology of these materials, according to a three-zone model, dynamic moduli of Vectra A950 show plateau- and transition-zone behavior, while PC exhibits terminal-zone behavior. The blends show only terminal-zone behavior at low Vectra A950 contents ( $\leq 50\%$ ) and terminal- and plateau-zone behavior at higher Vectra A950 contents. The relaxation time of Vectra A950 is much longer than PC and the blends have relaxation times greater than additivity. Both the complex and steady shear viscosities of the blends increase with the addition of Vectra A950. This is attributed to interfacial association, which retards the reorientation and alignment of the Vectra A950 phase in the molten state. The Cox–Merz rule holds true for PC but not for Vectra A950 and the blends. Free volume properties on an angstrom scale evaluated by positron annihilation lifetime spectroscopy (PALS) indicate that Vectra A950 has smaller, fewer free volume cavities than PC and the variation of free volume behavior in the blends can be explained in terms of blend miscibility. The measured densities of the blends agree well with the free volume fractions of the blends determined from PALS. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2319–2330, 2000

**Key words:** thermotropic liquid crystalline polymer; blend, miscibility; positron; free volume

## INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) are anisotropic materials possessing excellent thermal and mechanical properties. Compared to

their lyotropic counterparts, TLCPs have the advantage of being thermoplastic with accessible melting temperatures, and therefore traditional blending and compounding methods can be used. In order to reduce the impact of their relatively high cost on commercial uses, blends of TLCPs and thermoplastics (TPs) have been extensively studied. As often observed in low molecular weight liquid crystals, which only form miscible

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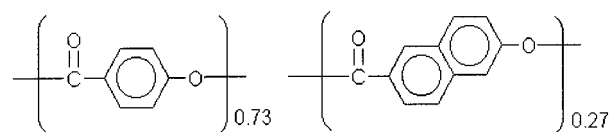
mixtures with liquid crystals of same packing characteristics,<sup>1</sup> the majority of blends containing TLCPs and TPs are immiscible.<sup>2-7</sup> It has been found that the potential benefits of addition of TLCPs in TPs can be dual, reducing the blend viscosity during processing and forming reinforcement in the TP matrix after the blend has solidified.<sup>8</sup>

Positron annihilation lifetime spectroscopy (PALS) has been demonstrated to be a potent technique to evaluate free volume properties in polymeric materials.<sup>9-11</sup> This technique involves the generation and annihilation of positrons (anti matter of electrons) and utilizes the positively charged nature of positrons that tend to be repelled by nuclei, and thus reside and decay in regions where electron density is low.<sup>11</sup> The lifetime parameters of *ortho*-positronium (*o*-Ps, a bound pair of a positron and an electron in the parallel spin state) are of most interest to polymer researchers as the lifetimes ( $\tau_3$ ) and probabilities ( $I_3$ ) of these *o*-Ps species decaying via a pick-off mechanism are found to correlate directly with the size and number concentration of free volume cavities, respectively.<sup>12,13</sup> PALS has been used, for example, to detect  $T_g$  and sub- $T_g$  relaxations by monitoring the temperature dependence of  $\tau_3$ .<sup>10,14</sup> Changes of properties of polymers resulting from molecular rearrangements such as physical aging also have been identified to show corresponding changes in PALS parameters.<sup>10,11,15</sup> Ramachandra et al.<sup>15</sup> used PALS to characterize physically aged poly(chlorotrifluoroethylene) and found that  $I_3$  decreased dramatically with aging time, indicating that physical aging increased the degree of chain packing. PALS work on polymers to date has been predominantly focused on neat TPs and blends containing only TPs.<sup>10</sup> Miscible TP/TP blends are usually found to have  $\tau_3$  (and thus free volume cavity sizes) smaller than additive values of the two constituents, which has been attributed to favorable interchain interactions and resultant close packing.<sup>16-18</sup>

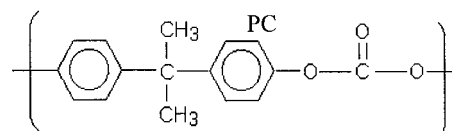
In the present work, blends of a wholly aromatic TLCP (Vectra A950) and polycarbonate have been studied with reference to their miscibility, rheology, and free volume behavior. Although similar blend systems have been studied,<sup>5-7</sup> the correlations between blend miscibility and microstructure such as free volume properties evaluated by PALS have not been reported and are of much interest.

## EXPERIMENTAL

The polymers used in this study include a nematic TLCP, Vectra A950, and a bisphenol-A type polycarbonate (PC). Vectra A950 (labeled Vectra hereafter) was supplied by Hoechst-Celanese. Vectra is a copolyester of 73 mol % *p*-hydroxybenzoic acid (HBA) and 27 mol % 2-hydroxy-6-naphthoic acid (HNA). The PC used was Lexan 134 and was obtained from GE Plastics, Australia. Their chemical structures are as follows:



Vectra A950



PC

A Haake Rheomix 600 mixer equipped with two sigma rotors was employed to prepare Vectra/PC blends of the following weight ratios: 10, 20, 30, 50, and 75% of Vectra. Vectra and PC were placed in a vacuum oven at 100°C to dry for 24 h before use to reduce potential hydrolysis during blending. Transesterification can occur between polyesters and polycarbonates during processing. As the emphasis of this work is on the physical mixing of Vectra and PC, a transesterification inhibitor, Irganox 1098, obtained from Ciba-Geigy, was incorporated with the polymer pellets (0.2% of total weight) to limit chemical reaction taking place during blending. The mixture was then further melt blended in the Haake mixer for 5 min at 320°C with a rotor rotation rate of 20 rpm.

Dynamic mechanical thermal analysis (DMTA) was carried out on a Rheometrics Dynamic Analyzer II (RDAII) equipped with torsion rectangular fixtures in a torsion mode. Measurements by RDAII were conducted every 2°C with a soaking time of 1 min to allow thermal equilibrium to be reached. DMTA was also undertaken on a Perkin-Elmer DMA-7 in a penetration probe mode with a heating rate of 2°C/min. A frequency of 1 Hz over

a temperature range from 50 to 180°C was employed in both instruments.

Thermal properties of the blends were measured by a DuPont 9900 thermal analyzer equipped with a differential scanning calorimetry (DSC) module. Samples of 10–15 mg were initially scanned over a temperature range from 50 to 300°C at a heating rate of 20°C/min and cooled to 50°C at a cooling rate of 20°C/min immediately after the furnace reached the final temperature. Samples were scanned again from 50 to 300°C at the same heating rate. The measurements were carried out in a nitrogen atmosphere with a gas flow of 60 cm<sup>3</sup>/min. The reported results were taken from the second heating runs to avoid the experimental artifacts arising from any previous thermal history.

Dynamic rheological characterizations of the blends were carried out on the RDAII in an environmental chamber at 320°C under nitrogen atmosphere. The measurements were performed within the linear viscoelastic region obtained by strain sweep test using 25 mm gap parallel-plate fixtures with a gap of 0.9 mm. Capillary shear viscosities of the blends were obtained by using a Galaxy III capillary rheometer with a capillary die of diameter 0.76 mm and length 25.4 mm (L/D = 33). The Rabinowitch correction for nonparabolic velocity profiles was applied to the capillary rheometer data.

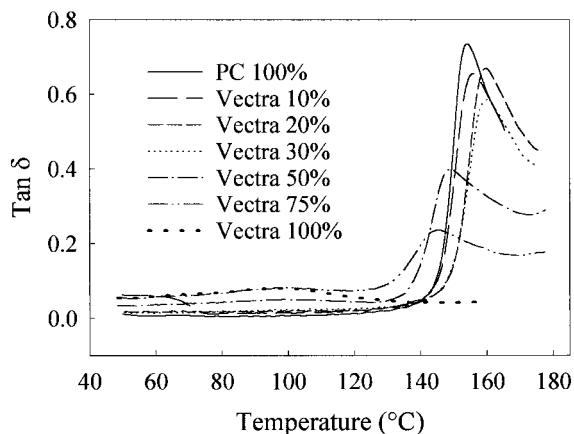
The PALS measurements were made on an automated EG&G Ortec fast-fast coincidence system using a <sup>22</sup>Na spot source. The equipment was thermally equilibrated in an air-conditioned laboratory maintained at 22 ± 1°C to avoid electronic drift. Further experimental details and theories related to the PALS technique can be found elsewhere.<sup>11</sup>

Density measurements of the blends were performed on a Micromeritics Accupyc 1330 gas displacement pycnometer. Blend samples were purged by helium ten times to ensure a consistent dry atmosphere on testing. The reported density of the sample was obtained from averaging ten measurements at ambient temperature under a helium atmosphere.

## RESULTS AND DISCUSSION

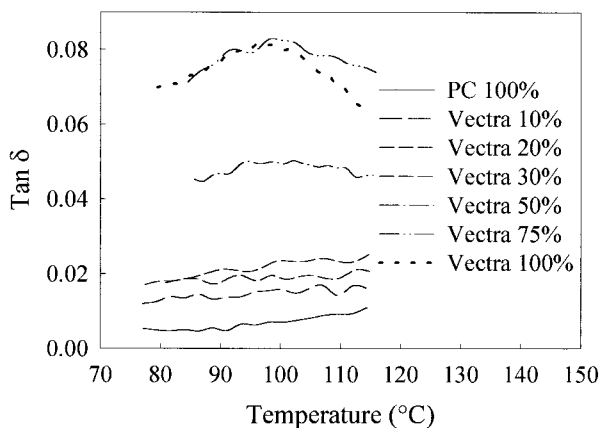
### Miscibility

The determination of the  $T_g$ s of polymer blends, either by the thermal or dynamic mechanical



**Figure 1** The  $\tan\delta$  spectra of the Vectra/PC blends determined by DMA-7.

method, is a generally accepted way to confirm the miscibility of polymer blends. Figure 1 shows the  $\tan\delta$  curves of the Vectra/PC blends by DMA-7. In a broad sense, the addition of Vectra causes the height of the  $\tan\delta$  peak of the PC component to decrease gradually. However, the  $\tan\delta$  peak of the blend moves to *higher* temperatures than that of neat PC for up to 30% Vectra content. It is not often observed that the blend  $T_g$  is greater than either of the constituents and that it increases with the addition of a constituent with a lower  $T_g$ . Gross phase separation (immiscible blends) is usually confirmed if DMTA results show two distinct  $T_g$ s at the same temperatures of the pure components and varying in peak height according to the component concentrations. In the case of miscible systems, a single  $\tan\delta$  peak that moves in proportion to concentrations of the constituents both in temperature and height from one component polymer to the other would be expected. Partially miscible blends typically show distinct  $T_g$ s of the blend components moving toward each other, with the heights of the peaks also in proportion to concentrations of the component polymers. The behavior observed in Figure 1 cannot be readily classified into any of these categories. In order to determine more precisely the miscibility of Vectra and PC, the  $\tan\delta$  curves of the blends near the Vectra  $T_g$  were closely examined. An enlargement of Figure 1 at the glass transition region of Vectra is shown in Figure 2. The very weak  $\tan\delta$  peaks of Vectra components in the blends can be observed, moving to slightly higher temperatures, and becoming flattened due to dilution effect, as the Vectra concentration decreases.



**Figure 2** The  $\tan\delta$  spectra of the Vectra/PC blends in the vicinity of Vectra's  $T_g$ .

Other than special situations such as intramolecular repulsion of a PS ionomer in its blends with Vectra,<sup>19</sup> most TLCP/TP blends reported in the literature have been generally found to be phase-separated. This is especially the case when a wholly aromatic TLCP is one of the blend components. This has also been the case for Vectra/PC blends, which have been reported to be phase separated in the blend systems of similar components.<sup>5-7</sup> As the  $T_g$ s of both components in out blends occur near the temperature locations of the pure polymers (despite the unusual behavior of the  $T_g$  associated with the PC component at low TLCP contents), the blends of Vectra and PC appear predominantly immiscible.

More specifically, an increase in  $T_g$  of the PC component has certainly not always been observed in other studies of blends of Vectra and PC.<sup>5-7</sup> Malik et al.<sup>5</sup> reported limited miscibility in the blends of Vectra and PC (Lexan130-111) processed at 280°C, supported by a slightly decreased  $T_g$  of the PC-rich phase measured by DSC. The  $T_g$  associated with the Vectra phase is rarely seen well in DSC thermograms. Turek et al.<sup>6</sup> studied the properties of a PC (Lexan 134)

blend containing 25% Vectra, and showed that the  $T_g$  of the PC-rich phase of the blend was slightly lower than that of the pure PC and there was a distinct Vectra  $T_g$  at almost the same temperature of neat Vectra. However, as with our work, Engberg et al.<sup>7</sup> studied blends of Vectra and PC (Lexan 141R) and the  $T_g$  relating to PC-rich phase increases with the addition of low- $T_g$  Vectra, up to 40% Vectra content. There was no mention of the  $T_g$  associated with the Vectra phase in these blends. This was probably due to the blends of the low concentration Vectra (up to 40%) studied, and that they used DSC, which could not clearly show distinct  $T_g$ s of rigid TLCP materials. They proposed that the occurrence of transesterification between Vectra and PC could lead to a stiffened PC phase, and therefore an increase of glass transition temperatures of the blends with Vectra content.<sup>7</sup>

For blends with higher Vectra contents (50 and 75% Vectra) investigated in this work, the  $\tan\delta$  peak temperatures of PC-rich phases are lower than that of pure PC and decrease with increasing Vectra content. This is more typical behavior of partially miscible blends as the  $T_g$  shifts slightly toward that of Vectra and the damping intensity decreases with increasing Vectra concentration.

In order to confirm the  $T_g$  behavior of these blends (especially the increase in  $T_g$  for blends with low Vectra contents), the  $T_g$ s of the blends were also determined by means of RDAII and DSC. Table I lists the values of  $T_g$ s of the Vectra/PC blends by various techniques. All three sets of the blend  $T_g$ s from different methods, although not with the same absolute values, show the same trend, i.e., increasing with Vectra content up to 20 or 30% and then decreasing upon further addition of Vectra. This result proves that the unusual  $T_g$  results of the blends at low Vectra concentrations are true material properties rather than an artifact arising from a particular measurement method or instrumentation. At this

**Table I**  $T_g$  Values of Vectra/PC Blends Determined from Various Techniques

	100% PC (°C)	10% Vectra-A (°C)	20% Vectra-A (°C)	30% Vectra-A (°C)	50% Vectra-A (°C)	75% Vectra-A (°C)	100% Vectra-A (°C)
DSC	155	156	158	155	151	146	—
DMA-7	154	156	160	160	149	145	99
RDAII	153	155	159	158	151	147	99

point, the source of such an increase is not totally clear. Engberg et al.'s suggestion of some transesterification leading to stiffening of the PC molecules is attractive.<sup>7</sup> Although, generally, transesterification between TPs may result in a  $T_g$  intermediate between them (as for miscible blends), a different scenario is possible to blends containing TLCPs and TPs. This relates to the fact that the  $T_g$  of the Vectra component is low, despite it being a rigid chain, the ordered packing of the LC state leading to a glass transition that is related to local shearing, transitional motions. Such motions are facilitated ( $T_g$  reduced) if there is good, close packing. However, if some rigid Vectra segments are incorporated into the more flexible PC molecules, greater chain rigidity (with no commensurate increase in order) would give rise to a higher  $T_g$ , as is observed. That is, the amount of incorporated Vectra material is small enough to cause an increase in PC-phase  $T_g$ , but far less than required to cause a LC-like alignment.

### Rheological Behavior

Figure 3 shows the dynamic moduli of the Vectra/PC blends at 320°C.  $G''$  of PC is greater than its  $G'$  within the frequency range studied [Fig. 3(b)], while Vectra exhibits greater values of  $G'$  in the low frequency region and greater  $G''$  at higher frequencies [Fig. 3(h)]. A three-zone model,<sup>20,21</sup> as shown in Fig. 3(a), is employed to interpret dynamic modulus curves of the blend system. According to the relative values of  $G'$  and  $G''$ , a log plot of dynamic moduli consists of terminal, plateau, and transition zone. The time scale associated with the terminal zone is thought to correspond to long-range relaxations (beyond entanglement distance), while the time scale of the transition zone is related to short-range relaxations (motions within entanglements).<sup>21</sup> Vectra shows both plateau- and transition-zone behavior in the frequency range studied, as has also been observed in other studies,<sup>22–24</sup> while PC exhibits terminal-zone behavior only. This indicates that Vectra has much longer relaxation times than PC as its terminal-zone behavior would be expected to appear in the very low frequency region (longer time scale), beyond the accessible frequencies of the RDAII. Their blends show only terminal-zone behavior up to 30% Vectra content, as seen in Fig. 3(b)–(d). Further addition of Vectra results in the terminal- and plateau-zone behavior of the blends. The dynamic rheological features of the

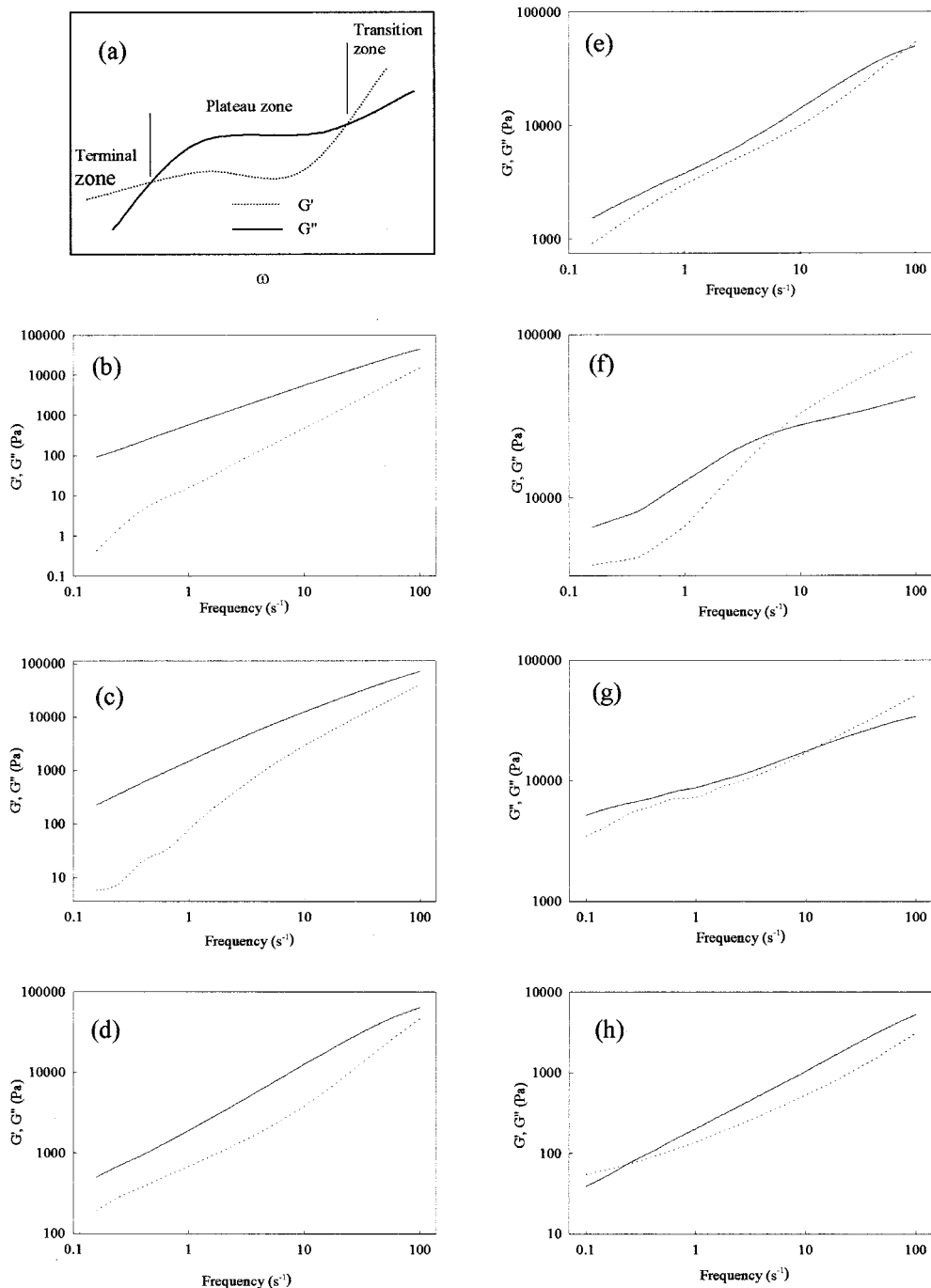
molten blend system are in good agreement with results in the solid state by DMTA. That is, the blend behavior is controlled predominantly by the PC component until the Vectra concentration reaches 30%. The influence of Vectra then comes into play (although not in a dominant fashion) at greater Vectra contents ( $\geq 50\%$ ).

Figure 4 shows the relaxation times ( $\lambda$ ) of Vectra/PC blends, calculated from dynamic rheological parameters by an empirical equation<sup>25–27</sup>:

$$\lambda = G' / (|\eta^*| \times \omega^2) \quad (1)$$

where  $G'$  is the storage modulus,  $\eta^*$  is the complex viscosity, and  $\omega$  is the applied frequency. At the frequency of 1 s<sup>-1</sup>, Vectra has a relaxation time orders greater than PC. At high frequencies such as 100 s<sup>-1</sup>, Vectra still relaxes much slower than PC, although the difference is far smaller than at 1 s<sup>-1</sup>. Relaxation times of TLCPs obtained from eq. (1) have been shown to be a few orders longer than that of the flexible chain polymer at low frequencies.<sup>26</sup> Even at high frequencies, TLCPs still exhibit relaxation times several times greater than flexible chain polymers,<sup>26,27</sup> since high frequency relaxation times may only be associated to the rearrangement of the shorter molecular segments similar to the relaxation process occurring in the transition zone.<sup>20</sup> The slow relaxation process of TLCPs can be attributed to the rigidity of the TLCP molecules and the planar molecular moieties of TLCPs such as phenylene and naphthalene units, which restrict the chain mobility.<sup>27,28</sup> The relaxation times of the immiscible Vectra/PC blends display a distinct, positive deviation from additivity that increases with increasing Vectra content up to 30% Vectra. The relaxation times of the blends with Vectra contents greater than 30% become comparable to neat Vectra. This composition range is consistent with the occurrence of partial miscibility of the blends. An assumption of good interfacial bonding of the immiscible Vectra/PC blends seems reasonable as the blend relaxation is clearly retarded by the existence of the Vectra component.

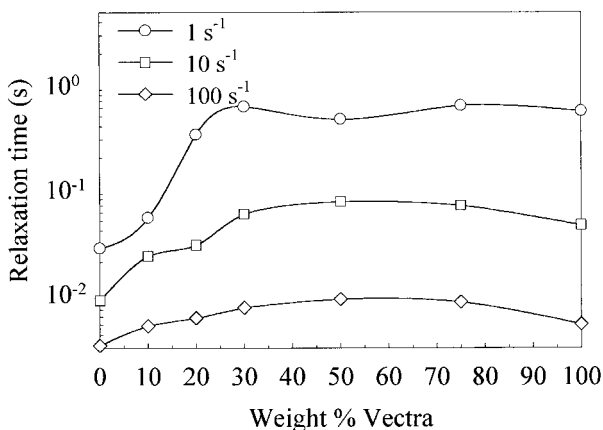
Figure 5 shows the complex viscosity of the Vectra/PC blends at 320°C. Vectra shows shear-thinning behavior, while PC displays a Newtonian plateau in which viscosity is independent of frequency within the frequency range studied. Although Vectra is less viscous than PC, the viscosities of the blends increase with the addition of Vectra. Blends with more than 20% Vectra show



**Figure 3** Dynamic moduli of the Vectra/PC blends at 320°C. (a) Three-zone model, (b) PC, (c) 10% Vectra, (d) 20% Vectra, (e) 30% Vectra, (f) 50% Vectra, (g) 75% Vectra blends, and (h) Vectra.

shear-thinning characteristic, which is clearly influenced by the Vectra component. Furthermore, despite being more viscous than the pure components, the blend viscosity appears to approach the PC value at the high end of frequencies due to an

increasing degree of shear thinning. The compositional dependence of the blend viscosity, as seen in the inset of Figure 5, is found to show positive deviations from additivity. This is most likely due to the morphological effect of the phase-separated



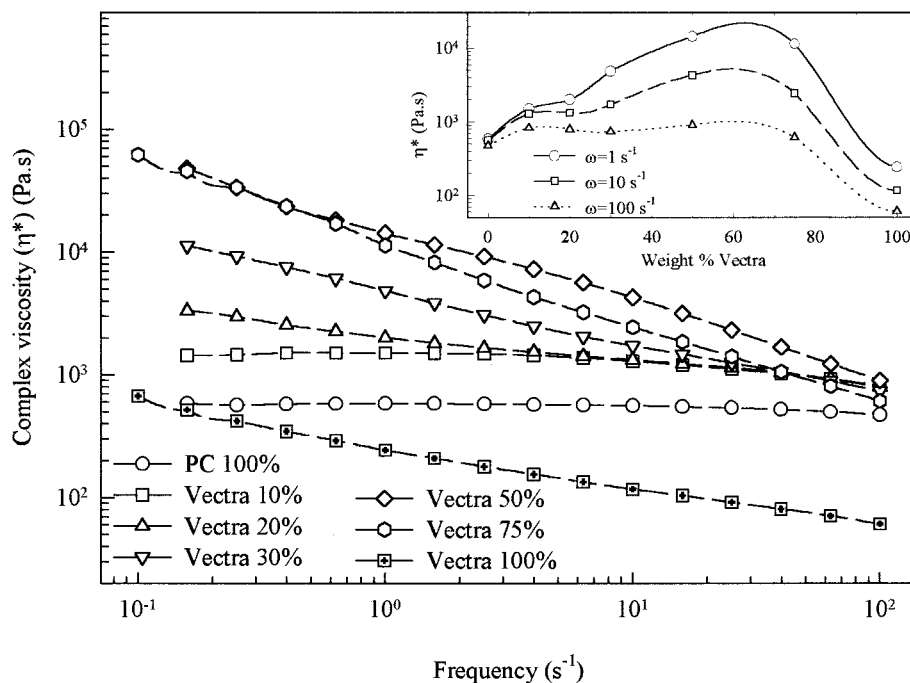
**Figure 4** Relaxation times of the Vectra/PC blends at 320°C, calculated from eq. (1).

blends than the intrinsic molecular nature of PC and Vectra.

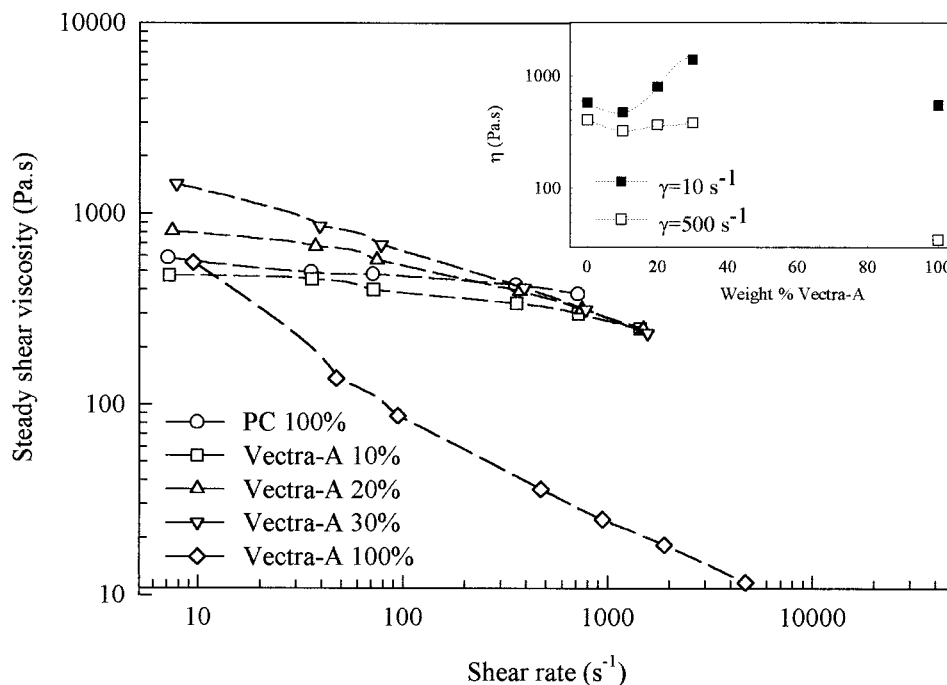
It has been found that immiscible TP/TP blends<sup>29-31</sup> and the immiscible TLCP/TLCP blends<sup>32</sup> often show positive deviations in the blend complex viscosity as a function of blend composition. Sodium (NaSPS) and polyamide 6 (PA6) formed immiscible blends that showed positive deviations at frequencies of 0.1, 1, 10, and 100 s<sup>-1</sup>.<sup>29</sup> By contrast, mixtures of lithium-sul-

fonated PS ionomers (LiSPS) and PA6 resulted in homogenous blends and the compositional dependence of complex viscosity of such blends showed the weighted average behavior at low frequencies and negative deviations at high frequencies.<sup>29</sup> Compositional dependence of complex viscosity of miscible blends of TLCP (HIQ45) and PC have been found to show sinusoidal variation around mean values.<sup>33</sup> Although factors governing the compositional dependence of complex viscosity for miscible or immiscible blends are not fully understood, they appear to be characteristic features of many polymer blends.

The steady shear viscosity of a limited set of the Vectra/PC blends at 320°C is depicted in Figure 6. PC shows Newtonian behavior and Vectra is strongly shear thinning, as in the oscillatory shear. Except for 10% Vectra blend, the viscosity of the blends increases with Vectra content at lower shear rates ( $\leq 300$  s<sup>-1</sup>), consistent with the oscillatory shear results. The influence of Vectra on the steady shear viscosities of the blends is also similar to oscillatory shear, the shear rate dependence of the viscosity curve becoming more shear thinning with higher Vectra concentrations. Compositional dependence of the steady shear viscosities of Vectra/PC blends is shown in the inset of Figure 6. At a shear rate of 10 s<sup>-1</sup>, PC



**Figure 5** Complex viscosities of the Vectra/PC blends at 320°C; inset: compositional dependence of complex viscosity.



**Figure 6** Steady shear viscosities of the Vectra/PC blends at 320°C; inset: compositional dependence of steady shear viscosity.

and Vectra have almost the same viscosities, while blend viscosity increases with the addition of Vectra (except for 10% Vectra blend). At a shear rate of  $500 \text{ s}^{-1}$ , although Vectra is far less viscous than PC, blends have roughly the same viscosity slightly below that of PC.

It has been reported that the steady shear viscosities of Vectra/PC blends show values intermediate to those of the component materials.<sup>5,6,34,35</sup> However, the steady shear results reported by Engberg et al.<sup>7</sup> agree well with Figure 6 in every aspect. They commented that the lack of viscosity reduction for the blends with addition of Vectra resulted from the occurrence of transesterification between Vectra and PC.<sup>7</sup> This leads to a stiffened PC phase, evidenced by an increase in the glass transition temperatures of the blends with Vectra content, which was also observed in this work (Fig. 1 and Table I) and discussed previously.

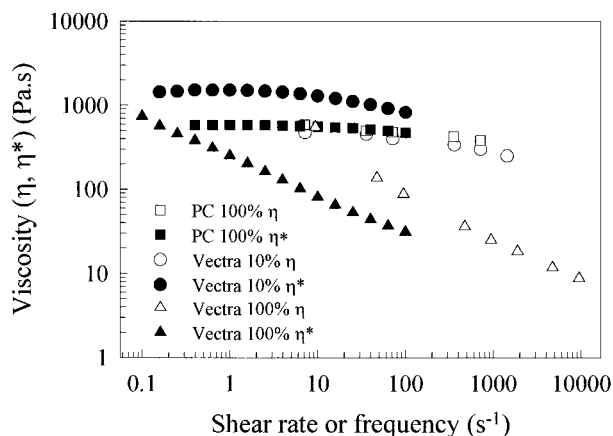
Transesterification among polyesters and/or polycarbonates has been known to depend strongly on processing temperature and blending methods.<sup>36</sup> In Engberg's work, the occurrence of transesterification between Vectra and PC was attributed to the higher temperature employed ( $335^\circ\text{C}$ ) in blending and the enhanced mixing of a twin-screw extruder.<sup>7</sup> In this study, the use of

internal mixer, which achieves a better mixing, is also likely to encourage transesterification. Although precautions have been taken to inhibit transesterification in this study, transesterification may not be totally eliminated during blending.

Transesterification may generate some block copolymers of Vectra and PC in the interfaces of the blends. These copolymers could function as a compatibilizer to improve the interfacial bonding for the phase-separated Vectra/PC blends. Compatibilized TLCP/TP blends have been reported to show viscosity recovery compared with their uncompatibilized counterparts,<sup>37-39</sup> although not necessarily leading to a blend viscosity greater than those of the pure components. A Vectra/PP blend with 30% Vectra content showed a significant viscosity reduction compared with pure PP, while the viscosity of the compatibilized blend was equivalent to that of the pure PP.<sup>37</sup> A compatibilized Noryl (a miscible mixture of PPO/PS = 50/50) blend containing 10% Vectra was found to be more viscous than the uncompatibilized blend and the pure components.<sup>38</sup>

The proposed morphology (a two-phase blend with good interfacial bonding) could be used to explain the increase of blend viscosity. It is well known that the strong shear-thinning nature of





**Figure 7** Comparison of complex and steady shear viscosities of the Vectra/PC blends at 320°C.

LCPs arises from their potential chain alignment with respect to shear and elongational forces.<sup>40</sup> However, if the dispersed Vectra domains are strongly associated with the PC matrix, it could lead to difficulty in domain reorientation, as well as Vectra chain alignment during flow. If the Vectra domains in the blends are fixed in certain directions and cannot readily reorient or be aligned in the flow direction due to strong interactions with the continuous phase, the blend viscosity would be expected to increase with the addition of Vectra. Higher shear rates ( $\geq 300 \text{ s}^{-1}$ ) appear to be able to weaken these proposed interfacial associations to some extent, because the blend viscosities are equal to or slightly lower than the viscosity of the matrix PC. They are, however, still much higher than that of the neat Vectra. This assumption of good interfacial bonding in the melt will be further investigated by examining the free volume behavior of the blends in the solid state.

The Cox–Merz rule predicts that the magnitude of the complex viscosity ( $\eta^*$ ) should be comparable with that of the steady shear viscosity ( $\eta$ ) at equal value of frequency ( $\omega$ ) and shear rate ( $\dot{\gamma}$ ).<sup>41</sup> Figure 7 gives the comparison between  $\eta$  and  $\eta^*$  of PC, 10% Vectra blend and Vectra at 320°C. PC appears to obey the rule well, whereas Vectra clearly shows a deviation. The empirical Cox–Merz rule has been shown to be applicable for flexible polymers, but it seems to be invalid for materials with ordered structures such as liquid crystalline materials and suspensions.<sup>42,43</sup> The immiscible blends of Vectra and PC do not follow the rule, as seen in Figure 7 where only the 10% Vectra blend is shown. It has been reported that

that the rule may not hold when morphological influences have to be considered.<sup>44,45</sup> Li et al.<sup>44</sup> characterized the rheological properties of different PP blends. In spite of both matrix materials obeying the rule, their immiscible blends with a maleic anhydride PP showed distinct disagreement attributed to gross phase separation. The influence of the morphological factor has been confirmed by other studies of two-phase polymer blends for which the Cox–Merz rule was not obeyed.<sup>45</sup>

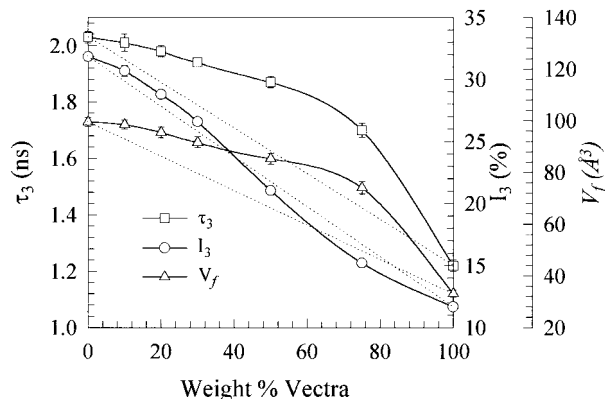
### Free Volume Behavior

Figure 8 displays the mean lifetime ( $\tau_3$ ) and intensity ( $I_3$ ) of *o*-Ps determined by PALS. By assuming a spherical free volume cavity, radii of free volume cavities  $R$  can be estimated by a semiempirical equation<sup>46</sup>

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1} \quad (2)$$

where  $R_0 = R + \Delta R$  where  $\Delta R$  is the fitted empirical electron layer (and equals 1.66 Å) from molecular crystals with known vacancy sizes. As  $\tau_3$  ranges from 0.5 to 3 ns, the mean radius of free volume cavities in polymers varies from approximately 1 to 6 Å.

An approximation volume of a free volume cavity  $V_f$  can thus be obtained if such a spherical geometry is assumed, once the radius  $R$  is known. From Figure 8, Vectra has  $V_f$  of 38 Å<sup>3</sup>, which compares well with values for other HBA/HNA TLCPs in the literature.<sup>47,48</sup> By contrast,  $V_f$  of PC is around 100 Å<sup>3</sup>, which is significantly greater than that of Vectra. It has been suggested that



**Figure 8** PALS parameters ( $\tau_3$ ,  $I_3$ , and  $V_f$ ) of the Vectra/PC blends.

free volume in TLCPs may tend to be “slit-like” rather than spherical<sup>47</sup> due to limited flexibility of TLCP molecules, and thus eq. (2) may be less valid. The blend  $V_f$  shows a significant positive deviation from additivity. The positive deviation from the additivity increases with increasing Vectra content up to 75% Vectra. Recall that in the case of miscible TP/TP blends, free volume of the blends has been observed to decrease in size (show a negative deviation with composition) due to intermolecular interactions which draw molecular chains closer together.<sup>16–18</sup> Therefore, it is reasonable to expect that immiscible blends may result in larger free volume cavities due to the repulsion of different molecular chains at interfaces. However, an increase in the sizes of the free volume cavities of the blends is seldom found.<sup>17</sup> Larger-than-average free volume cavities at the interfaces may skew the mean values of blend  $V_f$  to above-average values, even though the interfaces are likely to be good due to some transesterification. The immiscible blends are still likely to be less well packed than the neat components themselves. In addition, a small amount of transesterification may lead to difficulties in chain packing due to a more complicated molecular structure.

Alternatively, it is considered to be possible that positron and *o*-Ps prefer to form and/or diffuse to one of the phases in a multiphase blend.<sup>18</sup> Immiscible blends of Vectra and a polyetherimide, Ultem 1000, were found to have a negative deviation of  $\tau_3$  (and thus  $V_f$ ) from additivity. They attributed this behavior to a greater probability of *o*-Ps annihilation in the TLCP phase.<sup>48</sup> If such a diffusion occurs and given that the sizes of the free volume cavities in the blends in this work are close to the value of PC component, *o*-Ps annihilations in the Vectra/PC blends may take place predominantly in the PC phases and interfaces of the blends.

$I_3$  is a measure of the number of free volume cavities in polymers. As also shown in Figure 8, Vectra does not only have smaller, but also fewer free volume cavities compared with the flexible polymer, PC. Their blends show a positive deviation of  $I_3$  at low Vectra concentrations and a negative deviation at high Vectra concentrations from additivity, as seen in Figure 8. Although there has been no general conclusion drawn for the compositional dependence of  $I_3$  in the literature, it is logical to think that immiscible blends would show a positive deviation of  $I_3$ . It is likely that the interfaces between different phases may

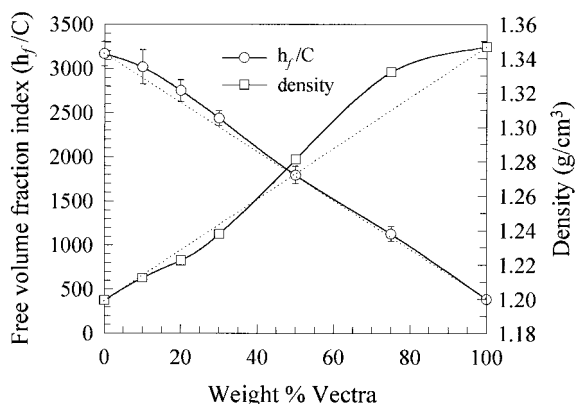
not only form larger free volume cavities (larger  $\tau_3$ ), but also create new ones. When the concentration of Vectra in the blend is below 30%, the blends are clearly immiscible, supported by the appearance of weak Vectra  $\tan\delta$  peaks in the  $\tan\delta$  curves of the blends (Fig.1). This slight positive deviation of  $I_3$  may indicate that the proposed good interfacial bonding counteracts the contribution of newly formed free volume cavities in the immiscible blends. The blends show partial miscibility of Vectra in PC at Vectra concentrations above 50%, as seen from the slight shift of the blend  $T_g$  associated with PC phase toward the  $T_g$  of Vectra (Fig.1 and Table I). A negative deviation of  $I_3$  at Vectra concentrations equal to or higher than 50% is observed. The compositional dependence of  $I_3$  seems to mirror miscibility: a positive deviation of  $I_3$  for blends with less than 30% Vectra (immiscible) and a negative deviation of  $I_3$  for blends with 50% and greater than 50% Vectra (partially miscible). Interfacial bonding of immiscible blends can be improved by the addition of a compatibilizer. Immiscible blends of LLDPE and isotactic PP were found to show  $I_3$  decreasing with increasing compatibilizer concentration.<sup>49</sup> This was attributed to the better interfacial packing and bonding of the LLDPE/PP blends since the fracture toughness of the blends also showed an improvement.<sup>49</sup>

Free volume fraction in polymers  $h_f$  can be estimated<sup>50</sup> from

$$h_f = C \times V_f \times I_3 \quad (3)$$

where  $C$  is an empirical constant determined from comparison with PVT data and is often found to be approximately  $1.8 \times 10^{-3}$  for flexible polymers. Because there are no  $C$  values available for TLCPs, a free volume fraction index  $h_f/C$  is used as an indication of free volume fraction in this work.

Figure 9 depicts the free volume fraction indexes  $h_f/C$  and the densities of the Vectra/PC blends as a function of composition. The free volume fraction index takes into account both the size and number concentration of free volume cavities of the blends.<sup>47</sup> The  $h_f/C$  indexes of the blends show a slight positive deviation up to 50% Vectra and additive behavior for higher Vectra contents. As the existence of free volume inevitably influences the density of polymers (a higher free volume fraction should result in a lower density), the correlation between  $h_f/C$  index and density is examined. It has been found that the cor-



**Figure 9** Free volume fraction index ( $h_f/C$ ) and densities of the Vectra/PC blends.

relation of  $h_f/C$  index and density of various polymers does not necessarily hold true.<sup>33</sup> For blends of the same constituents, the correlation is likely to be valid to some extent if there is no macroscopic structure defects formed in the blends larger than the angstrom scale accessible by *o*-Ps. For the Vectra/PC blends, the blend density is smaller than an average value when the blend possesses a free volume fraction greater than the average. The blends showing an additive  $h_f/C$  have densities much larger than average. This indicates that the blends with higher Vectra content ( $\geq 50\%$  Vectra) not only reduce the “PALS-detectable” free volume but also eliminate the free volume not able to be sampled by *o*-Ps.

## CONCLUSIONS

Blends of Vectra and PC were prepared by melt blending and their miscibility, rheology and free volume properties investigated. Although the  $T_g$  of the PC phase in the blends is slightly higher than that of neat PC and increases with the addition of Vectra up to 30%, the blends are found to be largely immiscible. This unusual increase in  $T_g$  of the PC phase is attributed to transesterification, which generates blocky copolymers of Vectra and PC and also results in modified, stiffened PC molecules.<sup>7</sup> The copolymer which results may play a role as a compatibilizer which improves interfacial miscibility of Vectra and PC.

Referring to a three-zone model of dynamic moduli, PC shows terminal-zone behavior, while Vectra shows plateau- and transition-zone behavior. As with the dynamic mechanical results in the solid state, the influence of Vectra on the zone

behavior of the blends occur at Vectra contents of 50% and greater. Both complex and steady shear viscosities of the blends increase with the addition of the less viscous Vectra. The difficulty in reorientation and alignment of Vectra phase in the blends during deformation may be the reason and occurs due to good interfacial bonding. The applicability of the classical Cox–Merz rule on the blend system was examined. PC is found to follow the rule, as generally observed for other flexible polymers. By contrast, the rule does not hold for Vectra nor the blends due to liquid crystalline order and/or morphological features.

Free volume properties probed by PALS reveal different characteristics for Vectra and PC. Vectra has fewer, smaller free volume cavities compared with PC because of its greater chain rigidity and closer packing. The blends have free volume cavities much larger than weighted averages. The compositional dependence of the number concentration of free volume cavities appears to correspond well with the blend miscibility, showing a positive deviation at low Vectra contents and a negative deviation at higher Vectra contents. This indicates that the newly created free volume at the interfaces due to immiscibility can be effectively compensated by improving interfacial bonding (due to transesterification). The compositional dependence of the free volume fractions, indicated by  $h_f/C$ , of the blends roughly follows additivity, with a slight positive deviation at low Vectra content region. Densities of the blends generally reflect the free volume fractions probed by PALS, having below average values at low Vectra contents and above-average values for higher Vectra contents.

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