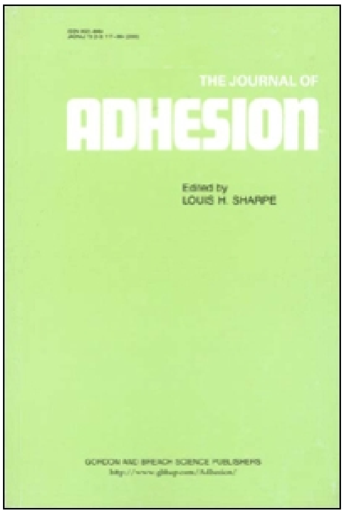

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Polycarbonate/TLCP Blends: Compatibilization, Barrier and Bond Characteristics

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Blends of polycarbonate and Vectra^{TM} liquid crystal polymer, at 88/12 weight ratios, have been prepared at temperatures ranging from 240-340°C. Inverse gas chromatographic data show that the bulk penetration of non-polar as well as polar vapors is significantly lowered in blends prepared above about 300°C. IGC data also report a surface excess of the TLCP component which was found to have a lower dispersion surface tension than the host polymer. The bond strength of PC/TLCP lap shear joints prepared over the noted temperature range increases monotonically with temperature, but a pronounced added change occurs in the 290-300°C interval. The results are consistent with earlier reports that at $T \geq 300°C$ PC and TLCP can interact only through dispersion (L/W) forces. Accordingly, it is apparent that a processability window exists for the blends in which the compatibility of the host and added polymer is enhanced, with repercussions on diffusion and bond characteristics.

Keywords: Polycarbonate; liquid crystal polymer; blends; preparation temperature; compatibility; diffusion; bond strength

1. INTRODUCTION

The problematic miscibility of thermotropic liquid crystal polymers (TLCP) with a range of commodity and engineering polymers has limited the promise of the TLCP family and launched studies into the causes of their limited miscibility. A valuable insight was given by

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Denn and coworkers [1], who found that in blends of the TLCP Vectra$^{\mathrm{TM}}$ with a polyester an apparent increase in the degree of compatibility was associated with annealing the blend at temperatures in the $\geq 300°\mathrm{C}$ range. Following on this, an earlier report from our laboratories [2] elaborated on the miscibility problem in polycarbonate (PC)/Vectra blends. The route followed was to characterize the surface interaction behavior of the polymers, using the methods of inverse gas chromatography (IGC) [3]. These showed the PC surface to be capable of interacting as both electron donor (base) and acceptor (acid), with the basic properties predominant. The chemical structure of the TLCP, involving carboxylic linkages, would have been expected to generate significant acid and base interaction properties. Surprisingly, however, the Vectra surface reported only very weak acid-base functionality [2]. Accordingly, it was implied that the polar groups were inward oriented, thereby contributing to the self-assembly characteristics of the polymer and leaving the surface able to interact primarily through long-range Lifschitz-van der Waals (L/W) forces. A major inference of the situation is that of weak bonding at the PC/TLCP interface. The same report [2] also included a study of the temperature variation of acid-base interaction constants for the polymers, with the interesting finding that in both PC and Vectra the acid-base (surface) functionality was thermo-labile. At temperatures above about 310°C the functionality was suppressed and the polymers would interact primarily through L/W forces, with the result of enhanced compatibility. This was similar to the findings of Denn *et al.* [1] and identified a processing condition for the production of more highly compatible, albeit metastable, PC/TLCP blends. SEM studies of blends prepared at 280°C and 320°C, that is above and below the "compatibility window", were consistent with the hypothesis showing significantly more interconnection between constituents of the blend prepared at 320°C than in its counterpart. The fundamental causes of temperature-dependent changes in blend compatibility remain uncertain, although a contributing factor may be the known and complex morphological changes in the TLCP polymer which occur in the vicinity of 300°C. Clearly, the suggestion of enhanced compatibility in PC/Vectra blends prepared at the designated elevated temperature required additional inquiry, which is the focus of this communication. Particular attention is given to the question of bond strength at

PC/Vectra interfaces prepared over temperatures encompassing the stated critical range. Enhancement of component compatibility should, in principle, favor component diffusion across the interface, leading to an increase in the interfacial bond strength. The matter is considered in terms of lap-shear bond strength measurements for joints prepared at the relevant temperatures. Also reported are results of a further application of the IGC method, in this instance to measure the diffusion of selected vapors through PC, TLCP and through blends of the polymers prepared at temperatures traversing the "processability window". The objective was to verify the notion that a change in the compatibility of the constituents would affect the barrier property of the blend, thereby affecting the adhesion characteristics.

2. EXPERIMENTAL SECTION

2.1. Materials

The host PC resin was a bisphenol A polycarbonate, Lexan^{TM} supplied by the General Electric Company. The TLCP, Vectra A 950, supplied by Hoechst-Celanese Corp., was a random 70/30 copolyester of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. Differential scanning calorimetry provided the data, already reported in [2]:

	T_g(°C)	T_m(°C)
PC	154	–
TLCP	106	284

2.2. Procedures

The polymers were studied individually and in blends with PC as the continuous phase and TLCP present at a concentration of 12 wt%. Prior to blending, all materials were devolatilized and dried under vacuum at 110°C for 8 h. Blending was done in a Brabender Plasticorder, with the mixing chamber controlled in the range 240–340°C under a flow of dry nitrogen. The rotor speed was constant at 60 rpm, and the duration at 4 min. Immediately following shear processing, the materials were plunged into liquid nitrogen and fractured cryogenically for use in IGC experiments.

2.3. IGC

IGC experiments were carried out with a Varian 3400 apparatus, equipped with both thermal wire and hydrogen flame detectors. To prepare stationary phases, the PC was deposited from 2% solutions in THF onto Chromosorb G, AW/DMCS, 60/80 mesh support, solvent evaporation taking place in a Rotovap unit. Conventional ashing analysis showed that the amount of supported polymer represented 9.4 wt% of the total mass. The TLCP and blend samples were crushed mechanically into flake form. All materials were housed in previously-washed and degreased stainless steel columns, typically 4.0 mm in diameter and about 50 cm long. The stationary phases were conditioned (in the Varian) for 24 h at 110°C under a flow of helium, prior to initiating measurements. The solids were probed at extreme dilution [3, 4] with *n*-octane (*n*C8), *n*-decane (*n*C10), tetrahydrofuran (THF) and chlorobenzene (CB). The alkanes represented vapors capable of interacting with the solid only through L/W forces. THF and CB are classified, respectively, as a base and an acid by the Gutmann convention [5]. These vapors, therefore, may interact with the solids through acid-base as well as L/W forces. Retention properties were measured at 130 and 160°C, near or above the Tg of the polymers. Under these conditions the vapors adsorb on the polymer surface and can then diffuse into the bulk [3, 6, 7], so that the measured net or total retention volume, $(Vn)_t$, is the sum of contributions from surface-adsorbed species and from vapor swept from the bulk of the polymer sample; thus,

$$(Vn)_t = (Vn)_s + (Vn)_b \tag{1}$$

where the subscripts s and b refer to the surface and the bulk, respectively. Various routes may be followed to separate $(Vn)_s$ and $(Vn)_b$. One of these, favored by some workers, is the capillary column technique [8, 9], in which the surface/volume ratio of supported polymer is systematically shifted upward. An alternative [7, 10] is to vary the flow rate of carrier gas so as to systematically reduce the residence time of the surface-localized probe molecule, thereby minimizing its chances of initiating diffusion into the bulk polymer. Following this concept in the present work, He carrier gas flow rates were varied from 5 to 70 mL/min. Retention times and volumes [3] were measured in at least triplicate, with deviations from means not exceeding 3%. Following the protocol described in earlier publications [7, 10]; explicit values of $(Vn)_b$ at finite flow rates were extrapolated to zero flow rate of carrier gas, to define a reference quantity $(Vn)_b^\circ$. This may then be used in a modified van Deemter equation to obtain a value for a molecular diffusion constant, D, from

$$(Vn)_b = (Vn)_b^\circ[1 - k\exp(-Dt)] \qquad (2)$$

Here k is a pre-exponential constant and t is the time the solute is adsorbed on the surface, as computed from the known retention time and volume at highest carrier gas flow rates. Either D or $(Vn)_b^\circ$ may be used as parameters describing the tendency of probe molecules of known size and interaction potential to penetrate into the polymer bulk. The use of this method on polymer blends represents an extension of the current data base.

2.4. Bond Strength

These experiments made use of lap-shear joints based on PC and TLCP specimens cut from compression molded sheets of the polymers. The initial molding temperatures were 300°C for the TLCP and 200°C for the PC. Rectangular samples cut from the PC sheets were 6.0 cm long, 1.5 cm wide and 0.10 cm thick. A pair of these formed the outer part of a sandwich for the TLCP, cut to 3.0 × 1.5 × 0.1 cm dimensions. The TLCP and PC were assembled so as to leave a 3.0 cm length of free PC at either end. The assemblies were placed between sheets of washed and dried aluminium and compression molded in a Carver Press. The press was controlled to ±8°C at temperatures in the range 240–340°C. The applied pressure was 1000 kg/cm^2, and the molding time was 1 min. Molded specimens were removed from the press and immediately plunged into cold, running water. Bond strengths were estimated with an Instron table model tester, operated at a jaw separation speed of 10 mm/min. From 3–5 joints from each molding temperature were evaluated, and the reported means have a deviation of ±8%.

3. RESULTS AND DISCUSSION

3.1. IGC

Chromatographic analysis was restricted to the pure PC and TLCP and to blends processed at 280° and 320°C, that is below and above the 300–310°C range in which the acid-base interaction potential of the homopolymers was shown to be strongly abated [2]. For convenience, the blend prepared at 280°C is labelled B-1 and that at 320°C, B-2. At 130–160°C, the temperatures used for IGC study, bulk absorption of injected probes into the polymer bulk is to be expected, since these temperatures were at or above the respective Tg values. Accordingly, the Vn values would vary with the carrier gas flow rate, F, in contrast to the situation below the polymer Tg. At lower temperatures Vn is independent of F in the most frequently used range of 5–20 mL/min; indeed, the independence is one of the criteria applied to the gathering of relevant retention data. The case of PC serves as a good illustration of the principle, Panzer and Schreiber [11] having found Vn for this polymer to be independent of F in $5 < F < 30$ mL/min. In the current work the expected flow rate variation was detected for all stationary phases studied. An illustration is given in the sections of Figure 1. Section (a) of the figure presents data for the host PC at 160°C. For each of the probes a well-defined plateau value was established, defining the $(Vn)_s$ datum. In the (b) section are given the corresponding results for B-2, again leading to well-defined $(Vn)_s$ for each of the injected probes. Extrapolations by curve-fitting to $F = 0$ then define the $(Vn)_t$ values and, thus, also the $(Vn)_b^\circ$ required for an application of Eq. (2). The sections of Table I present relevant data for the systems under study. The temperatures for reporting data in section A were chosen so as to maintain constant the ratio T/Tg.

A number of significant conclusions may be drawn from the tabulation. First, section A shows that PC is a much more interactive polymer than the TLCP. The $(Vn)_s$ are consistently greater. The nC_{10}

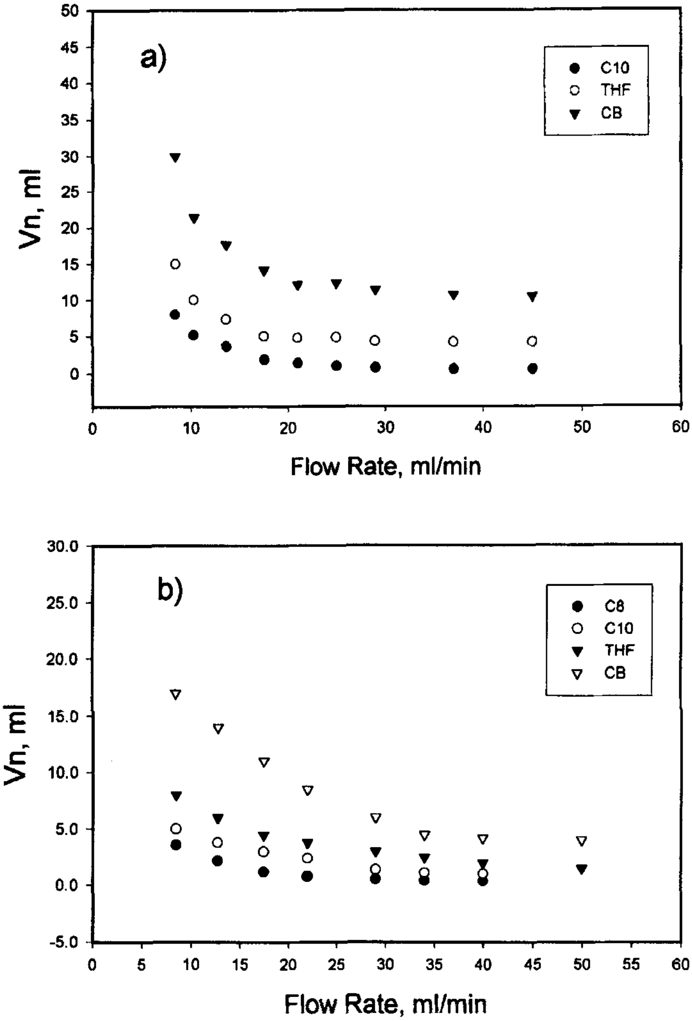

FIGURE 1 (a) Variation of net retention volume with carrier gas flow rate for PC polymer at 160°C; (b) Variation of net retention volume with carrier gas flow rate for blend B-2 at 150°C.

results indicate the presence of a stronger L/W force-field than in the self-assembled TLCP. The basic THF and acidic CB probes are even more strongly differentiated. As shown in Ref. [2], the acid-base interaction constants for the TLCP at 150°C ($Ka \simeq Kb \simeq 0.1$) are very

TABLE IA Retention and diffusion parameters from IGC measurements

Polymer:		*PC*			*TLCP*			*B*-1			*B*-2	
IGC @oC:		160			130			150			150	
	$(Vn)_s$	$(Vn)_b^\circ$	D	$(Vn)_s$	$(Vn)_b^\circ$	D	$(Vn)_s$	$(Vn)_b^\circ$	D	$(Vn)_s$	$(Vn)_b^\circ$	D
Probe: *n*C8							0.20	6.80	1.75	0.20	5.5	2.52
*n*C10	0.50	16.5	0.42	0.20	2.10	4.11	0.40	11.8	1.19	0.30	7.6	2.01
THF	4.1	17.0	0.48	0.20	1.33	5.90	0.50	12.9	1.29	0.30	10.7	1.45
CB	10.0	27.0	1.71	0.40	1.50	5.00	4.5	22.2	1.55	3.80	19.5	1.87

TABLE IB Surface energies and computed effective surface concentrations of TLCP

Polymer:	*PC*	*TLCP*	*B*-1	*B*-2
γ_s^d(mJ/m^2)*	19.5	14.7	–	–
$(Vn)_{scalc}$ from**:				
C10	–	–	0.46	0.46
THF			3.63	3.63
CB	–	–	9.28	9.28
Effective Surface Concentration $[TLCP]_e$ (%):				
From *n*C10			33	67
THF			94	98
CB			57	64

Notes: *All γ values at 150°C.
**Computed from $(Vn)_{scalc} = 0.88\ (Vn)_s$ PC$+0.12\ (Vn)_s$ TLCP.

small. Not surprisingly, non-dispersion (acid-base) forces add very little to the polymer's surface retention capabilities. PC at these temperatures reports Ka and Kb values an order of magnitude greater [11], Kb predominating. Again, this is reflected by the present results, with the acidic probe more voluminously held than the THF. The technique used here considers the $(Vn)_s$ value to be constant, unchanged by the varying carrier gas flow rates. This would be strictly correct were the surface sites of uniform energy. In fact, however, most polymers studied display a surface site energy variation of 5–10% [7]. Thus, the tabled data, based on the injection of limited quantities of probe molecules, tend to characterize the more energetic of polymer surface sites. The error incurred by assuming $(Vn)_s$ to be constants, however, is acceptable for the present requirements. Further, the experimental values for blends B-1 and B-2 are lower than they should be if the TLCP were uniformly distributed in the continuous PC phase. This is made clear in section B of the table by comparing the experimental values with those calculated on the assumption of uniform, stoichiometric distribution of components. The comparison suggests a strong preferential concentration of the TLCP in the surface layer, a stipulation supported by the γ_s^d data. The lower value for the TLCP creates a thermodynamic reason for that component to be preferentially surface-localized [12]. The apparent TLCP concentrations drawn from the retention characteristics of three probes are reported in the bottom section of Table IB. The most reliable result is that for the decane probe, since this is free from the selective retention of acid and base probes by their opposites in the surface sites. The apparent concentration of TLCP in B-1 is, therefore, near 33%, and in B-2 near 66%. The difference may be attributed to smaller and more evenly-distributed minor phase regions in the blend prepared under conditions where the polymers are more compatible [13]. The morphological and rheological changes characteristic of Vectra at the higher temperature, noted earlier in this paper, may contribute to the more effective migration of the component to the surface region.

The $(Vn)_b^\circ$ data indicate that the bulk distribution of components also is non-uniform. The main point of interest, however, is the comparison between the parameter values of the two blends. B-1, prepared below the temperature for the "compatibility window", absorbs each of the three probes more voluminously than does B-2, prepared within the temperature region of enhanced component compatibility. As already shown by SEM data [1], the bridging between continuous and dispersed phases is superior in that blend. The morphological difference between the blends would result in void volumes of reduced size and number, with the consequence of better barrier properties. Similarly, the D parameters distinguish between the two blends for each of the probes, assigning superior barrier effects to B-2. Thus, the weight of evidence from the IGC data source supports the contention that abatement of acid-base interactions at elevated temperatures for the PC/TLCP pair enhances polymer compatibility with a consistent consequence on the blends barrier property. Enhanced compatibility should promote the diffusion of TLCP and PC chains across the interface, thereby supporting the expectation that stronger interfacial bonds should exist in joints prepared at temperatures above the "compatibility window". The following section elaborates on the matter.

3.2. Bond Strength

The measurements reported here test the enhanced adhesion posit and also constitute an independent data source to question the existence of the putative "compatibility window" for the PC/TLCP blends of this inquiry. A direct measurement of bond strength seemed a reasonable choice. Accordingly, as stated earlier in this paper, lap-shear joints were prepared at temperatures straddling the "compatibility window", and the results of the investigation are presented in Figure 2.

The pattern of results follows expectations. For the major portion of the temperature range the bond strength of joints rises slightly and systematically. For joints prepared in the range 240–290°C an average value for this is 0.26 N/°C. A similar increment in bond strength, 0.24 N/°C, is observed in the 300–340°C interval. Between 290 and 300°C, however, there is a discontinuity in the pattern, the bond strength changing by about 40 N. This is more than an order of 10 greater than would have been expected from the systematic variation observed elsewhere in the range. It seems reasonable to associate the abrupt rise with the proposed enhancement of compatibility between the contacting polymers. The origins of the underlying minor bond property variation cannot be identified at this point, although a likely

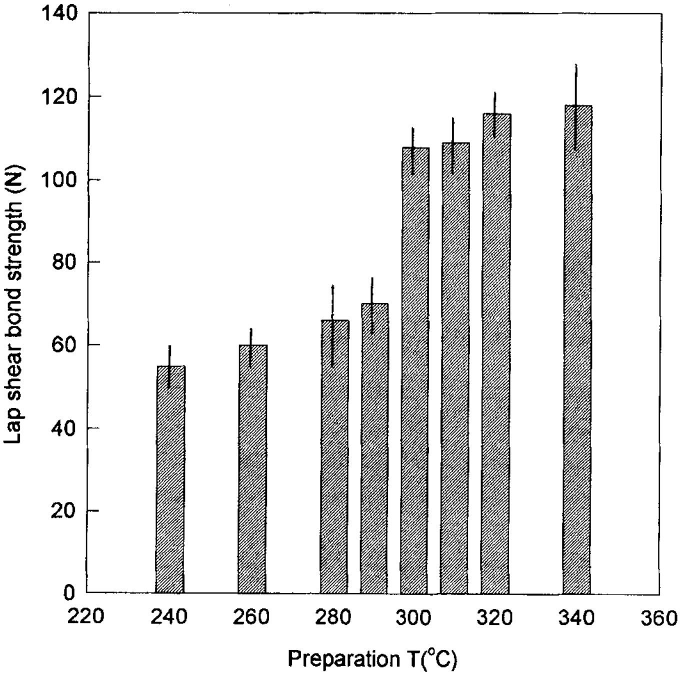

FIGURE 2 Lap shear bond strength (25°C) of PC/TLCP (88/12) blends prepared at various temperatures.

candidate is a change in the viscoelastic properties of the polymers. Rheological data, specifying viscosities and polymer elasticities, are needed to clarify the issue. These will be reported in a follow-up communication.

Finally, it follows that the enhanced compatibility conferred to the blends when processed at the temperatures identified here, is metastable. At lower temperatures, such as those used in the IGC and the lap-shear experiments, a reversion to the dispersion states appropriate to those temperatures must occur. The kinetics of the reversion process will, of course, depend critically on temperature. Thus, the bond strengths, measured under ambient conditions and far below the *Tg* of the polymers, may be expected to persist for lengthy periods. The IGC data, and parameters drawn from them, were collected nearer the polymer *Tg*. These may be more subject to time-dependent changes, a subject worth considering in greater detail in a future study. In the present case, the time required for collecting IGC data was kept as short as possible and reproducibility of datum points taken over a period of tens of minutes was excellent. Little significant morphological change could have occurred, so that the IGC and diffusion data may be regarded as reflecting reasonably the properties of blends prepared under conditions of the "compatibility window".

4. CONCLUSION

The following conclusions are drawn from the research:

- The apparent compatibilization of PC/TLCP (Vectra) blends, when they are processed at temperatures above 300°C, and ascribed to the abatement of unfavorable specific interactions, has been examined *via* the barrier properties and the adhesive joint strengths of the blend.
- The bulk retention of alkane, acidic and basic vapors by an 88/12 PC/TLCP blend is markedly reduced when the blend is processed at or above 300°C, consistent with the compatibilization concept.
- An excess of the TLCP component appears to be surface localized in the blends. The lower surface energy of the TLCP as compared with the PC matrix is cited as the thermodynamic cause of the effect.

- Lap-shear bond strengths of PC/TLCP joints increase slightly and systematically with processing temperature in the range 240 – 340°C; however, a significant added effect is observed in the 290 – 300°C interval, consistent with the hypothesis of enhanced compatibility of the polymers when processed at this temperature.

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