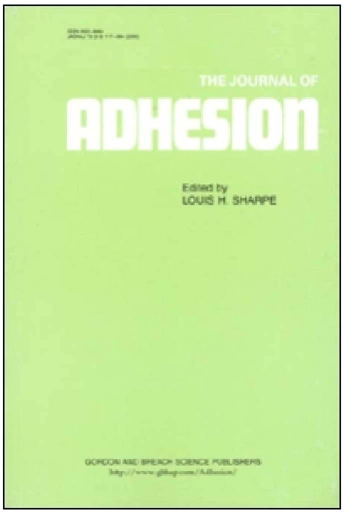

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Surface and Interaction Characteristics of Liquid Crystal Polymers and their Miscibility with Thermoplastic Hosts*

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Inverse gas chromatographic measurements have shown that the surface of thermo-tropic liquid crystal polymers, (TLCP), are capable of mainly dispersion force (L/W) interactions, with only slight contributions from non-dispersion (acid-base) forces. Structural moieties capable of non-dispersive interactions are primarily oriented into the TLCP bulk, perhaps accounting for the self-assembly effects in these polymers. Moreover, non-dispersive surface forces were found to be thermolabile, so that above characteristic temperatures only L/W forces remain. Blends of TLCP with polycarbonate and poly-etherimide hosts prepared below the characteristic temperatures displayed morphology typical of immiscible blends. When prepared at, and quenched from, temperatures above the pertinent characteristic value, electron micrographs showed evidence of adhesion at matrix/TLCP contacts, simulating the behavior of more miscible systems.

Keywords: Thermotropic liquid crystal polymers; blends; inverse gas chromatography; acid-base forces; miscibility

INTRODUCTION

This paper is dedicated to Robert Good, whose work has served as inspiration to his many colleagues.

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*One of a Collection of papers honoring Robert J. Good, the recipient in February 1996 of *The Adhesion Society Award for Excellence in Adhesion Science, sponsored by 3M.*

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The wide interest in thermotropic liquid crystal polymers (TLCP) [1] is due, in substantial part, to their ability to improve the processability of thermoplastic matrix polymers and, in some instances, to improve certain mechanical properties of the solidified blends. The improvement in processability has been reported on many occasions [2–6]. It is the result of viscosity decreases, notably at high shearing rates, when TLCP is added to host polymers, typically in the range from 5–30 wt.%. This behavior is characteristic of immiscible polymer systems [6, 7, 8]. The inherent immiscibility of TLCP/thermoplastic blends suggests the existence of weak interfaces, a factor that frequently compromises the ultimate usefulness of this class of material by making the mechanical properties strongly dependent on details of processing conditions [6, 7]. The situation also draws attention to the need for understanding the surface properties of TLCP and, thus, their behavior at interfaces and interphases with host polymers.

In an earlier publication from this laboratory [9], we have applied the method of inverse gas chromatography (IGC) to show that the specifically-interacting moieties of TLC polymers tend to be oriented into the bulk of the polymer, leaving the surfaces able to interact largely through weaker dispersion forces. This may account at least partly for the sensitivity of properties to details of processing conditions, since these will determine the degree of success in overcoming the self-assembly tendencies of the TLCP and, thus, its ability to disperse effectively in the matrix medium. The present work elaborates on the theme. Surface characteristics have been determined for specified TLCP and high melting point (engineering) thermoplastics by IGC and by static contact angle methods. The resulting data for surface free energies and specific (acid-base) interaction potentials have been obtained over a wide temperature range, extending into that normally associated with processing. An attempt is made to relate these physico-chemical aspects of surface and interface behavior with the morphology of blends where polycarbonate and polyimide are the hosts.

MATERIALS AND METHODS

The TLCP used in major portions of this work was Vectra® A 950 (V), supplied by Hoechst-Celanese Corp. This is a random copolyester of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. In certain cases a second TLCP, Rhodopol^{TM} was used; this crystalline polyester copolymer was supplied by Rhone Poulenc Corp. and is coded RP. Engineering thermoplastics used as polymer hosts were a bisphenol A polycarbonate (Lexan^{TM}) (PC), and a polyetherimide (Ultem^{TM} 1000) (PI), both from the General Electric Co. Differential scanning calorimetry, using a DuPont thermal analyser and a ramp of 10°C/min, yielded the following values for glass transition and melting temperatures:

	T_g(°C)	T_m(°C)
V	106	284
RP	175	328
PC	154	–
PI	220	–

The Polymers were studied individually and as blends in which PC and PI were the hosts and TLCP was present at 5, 10 and 20 wt.%. Prior to blending, all materials were dried and devolatilized under vacuum at 110°C for 8 h. A Brabender Plasticorder was used for blend preparation; the mixing chamber was controlled at temperatures in the 280–320°C range, the rotor speed was 60 rpm and mixing was continued for 4 min. Blends were transferred immediately to liquid nitrogen and specimens were fractured cryogenically for morphology analyses. These were based on scanning electron microscopy (SEM) involving a JEOL JSM 280 apparatus, at an acceleration voltage of 15 kV. Sample surfaces were overcoated by a sputtered gold layer.

IGC: Comminution of TLC polymers took place at the liquid nitrogen temperature. The particles (3.2 g of V and 6.5 g of RP) were packed directly in previously-degreased, washed and dried stainless steel columns 0.6 cm in diameter and about 0.5 m in length. PC and PI were deposited onto Chromosorb G (AW/DMCS treated, 60/80 mesh) support from chloroform solutions. Standard assay procedures [10] showed that the supported PC and PI represented 6–7% of the total mass.

Chromatographic measurements were made with a Varian 3400 chromatograph, equipped with both hot wire and hydrogen flame detectors. Dispersion force probes were the linear alkanes from *n*-hexane to *n*-nonane. Probes able to interact through acid-base forces were selected according to the classification of Gutmann [11]: Diethyl ether (DEE) and tetrahydrofuran (THF) were the basic (donor) probes, the acidic (acceptor) probes were ethyl acetate (EA) and chloroform (CL), while acetone (A) was chosen for its amphipatic properties. All vapors were injected at "infinite" dilution. The carrier gas was helium, at flow rates in the interval 10–30 mL/min. Reported values of the retention volume are averages of at least 3 separate runs, with a reproducibility better than ± 3%. IGC data were collected over broad temperature ranges allowing for significant overlap, as specified in Table I. Prior to making measurements, the various columns were conditioned in the apparatus under a helium flow at the maximum temperature applying to each of the solids.

Contact Angles (CA)

CA measurements were made with a Rame-Hart goniometer at 20°C. Polymer surface samples for these analyses were obtained by compression molding previously dried powders (10 h, 110°C under vacuum) into sheets, at a temperature 10° above the relevant Tm. Molded specimens were quenched immediately in cold water. Surfaces were cleaned with acetone and isopropanol and again vacuum dried. The standard series of wetting liquids (*n*-dodecane, formamide, glycerol, glycol, tricresol phosphate, and water) was used for CA determinations. The procedure elaborated earlier [12] to minimize the possible effects on contact angles of polymer/fluid interactions was applied to obtain the reference contact angle at zero contact time.

RESULTS AND DISCUSSION

i. The IGC data have been used to calculate the dipersive contribution to surface free energy, (γ_s^d), of the stationary phase, and its acid and

TABLE I Temperature range used in IGC measurements

Material	*Temp. Range*, °*C*
V A-950	60–260
RP	110–220
PC	80–175
PI	110–240

base interaction constants, Ka and Kb. The equations required for these purposes have been fully discussed in recent publications [13, 14, 15]. The surface free energy parameter was calculated from the equation

$$\mathrm{RT}\ln V_n = 2N\,a(\gamma_l{}^d)^{1/2}\cdot(\gamma_s{}^d)^{1/2} + C \qquad (1)$$

where V_n is the net retention volume, N is the Avogadro number, a is the crossectional area of the adsorbed probe molecule, $\gamma_l{}^d$is the dispersion component of the probe's surface free energy in the liquid state, C is an integration constant and RT have their usual meaning. The convention introduced by Lavielle and Schultz [14] to evaluate a was applied in this case. Eqn. (1) calls for linearity in a plot of its left hand side against the product $a\cdot(\gamma_l{}^d)^{1/2}$, when only dispersion-force vapors (here the *n*-alkanes) are involved. Depending on the solid's capacity for interaction through electron donor-acceptor mechanisms, the relevant acidic and basic probes will be more or less distant from the reference line. That distance can be equated to the acid-base contribution to the free energy of adsorption of the relevant probe, ΔG^{ab} [14, 15]. Since IGC data have been obtained over a specific temperature range, it follows that the adsorption enthalpy, ΔH^{ab}, is accessible from a plot of $\Delta G^{ab}/T$ *vs.* $1/T$. Gutmann's tabulation [11] provides the characteristic electron acceptor and donor numbers, AN and DN, of the volatile phases. We now follow the development detailed in Refs. [13, 14, 15] and introduce the acid and base interaction constants for the stationary phase, Ka and Kb respectively, through

$$-\Delta H^{ab} = \mathrm{KaDN} + \mathrm{Kb\,AN^*} \qquad (2)$$

In this expression AN* is a corrected value of Gutmann's AN, as proposed by Riddle and Fowkes [16]. Eqn. (2) provides access to the polymer's acid/base interaction constants.

The applicability of Eqn. (1) to present data is illustrated in Figure 1 by the results for RP at 110°C. The figure is fully representative of other relationships generated in the present study. The linearity defined by the dispersion probes is excellent, allowing the surface free energy parameter to be determined with good accuracy and precision. Both for *V* and RP, the acidic and basic probes fall slightly off the

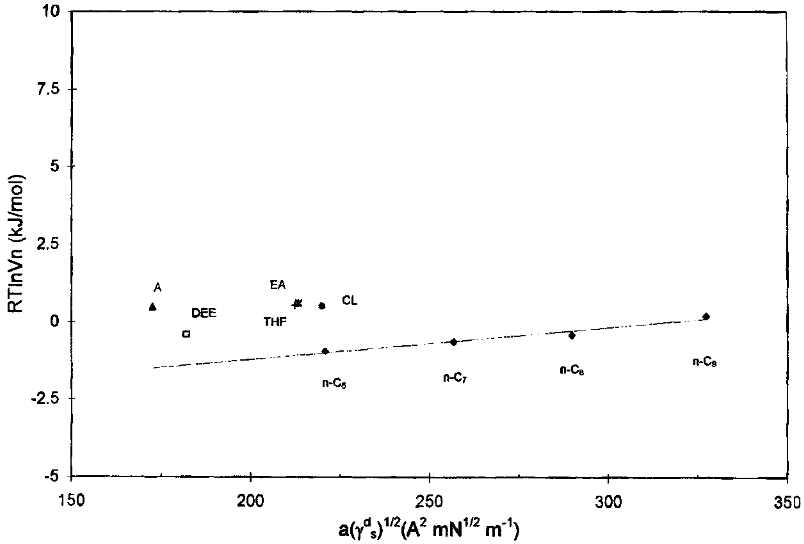

FIGURE 1 IGC data for RP polymer at 110°C.

alkane reference line, indicating the TLCP to be very weakly interactive and amphipatic. The available, detailed, set of results for V allows for the representation of the polymer's γ_s^d as a function of temperature. This is shown in Figure 2. The relationship is very complex, showing several transition temperatures. At temperatures below T_g, our surface energy values, in the vicinity of 40 mJ/m^2, are in very good agreement with earlier, independently obtained results [9]. The break from linearity in the 108–110°C range is attributed to the principal glass transition, in close agreement with the DSC determination of 106°C. Above the principal T_g are discerned additional transitions. A relatively minor one near 160°C is of unknown origin. The major one at about 190°C may be associated with phase orientation. The 230°C signal appears to relate to the ability of this polymer to crystallize from supercooled melts, as reported by Blizard and coworkers [17] and by Chapleau *et al.* [18]. These workers found the resulting crystals to melt in the 230–240°C range, well below the principal melting temperature and in good agreement with the present result.

The potential for acid/base interaction of TLCP surfaces is limited, as suggested by the results of Figure 1. That potential is further reduced

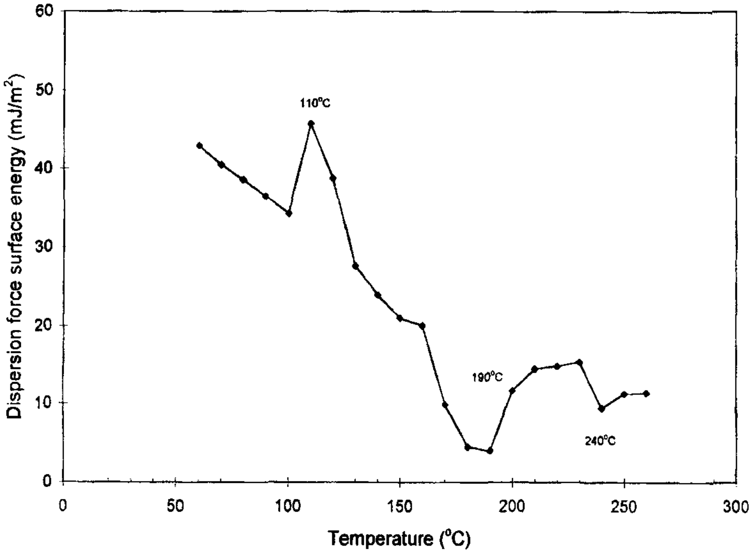

FIGURE 2 Showing the temperature variation of dispersive surface energy for Vectra TLCP.

at higher temperatures, as shown in Figure 3 for Vectra. Here, the retention volumes of acidic, basic and amphipatic probes is shown to decrease significantly as the temperature rises from 60 to 260°C. The implied possibility that acid/base forces may be thermolabile was raised in an earlier publication [9]. It seems reasonable that short range interaction forces would be perturbed by an increase in the kinetic energy of polymer chains, eventually leading to the situation where the residence time of a volatile probe on the mobile polymer site was insufficient to qualify as an adsorption event. Limiting temperatures for the persistence of acid/base effects would vary with the number and energy of interaction sites, and with the inherent magnitude of specific interaction for any donor/acceptor pair.

The above arguments are elaborated in terms of the polymer Ka and Kb constants. These have been calculated with Eqn. (2) for intervals of 30°C, and plotted against temperature in Figures 4 and 5 for *V* and RP, respectively. The amphipatic character of *V* is evident in that Ka and Kb values are essentially equivalent. Both parameters decrease with rising temperature, intercepting the abscissa near 360°C, at

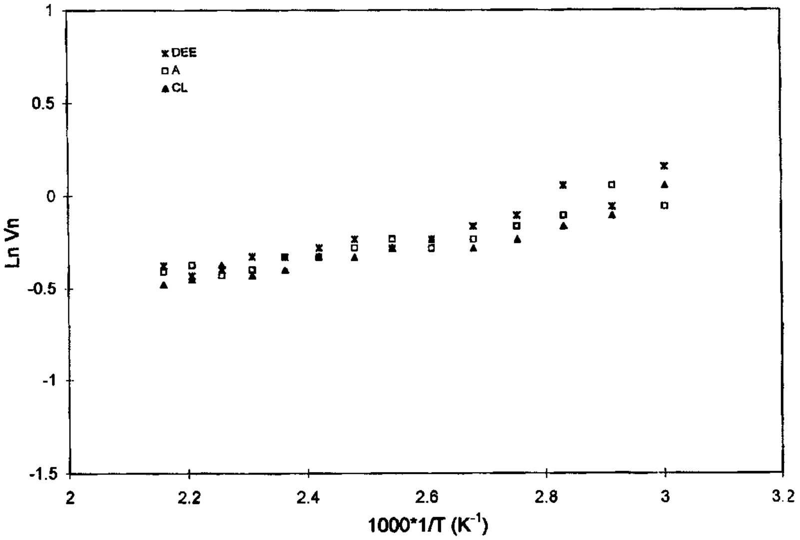

FIGURE 3 The temperature variation of retention volumes for polar probes interacting with the Vectra surface.

what is termed a critical temperature, T_c. Allowing for an experimental uncertainty of about 0.05 in Ka and Kb, however, indicates that the contributions to interactions arising from acid/base forces will, in the case of Vectra, become negligible above about 310–320°C. The case of RP is very similar. This TLCP is also weakly interactive, with a slight prevalence of acidic interactions, indicated by the consistently higher Ka values. In this case, acid/base interactions should become negligible above the T_c of about 300°C.

ii. The CA data provide support for the contentions made above. While the determination of contact angles is limited to the ambient temperature, sample surfaces can be conditioned at higher temperatures so as to simulate the IGC procedure. This has been done by exposing TLCP samples prepared for CA analysis to temparatures extending to 260°C. The exposure took place in air ovens, and was followed immediately by a liquid nitrogen quench. In this way we intended to immobilize the polymer in the state attained at the conditioning temperature. The sample cleaning and drying procedures, already described, were used and the thermally-conditioned surfaces

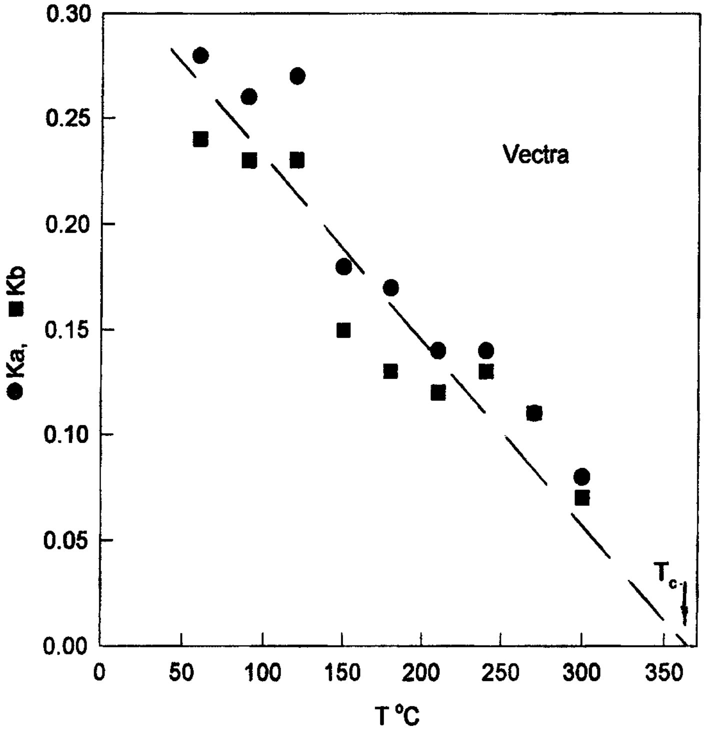

FIGURE 4 Temperature dependence of acid and base interaction parameters for Vectra TLCP, showing the thermolability of the acid-base interaction potential.

were then used for CA analysis. Through use of the harmonic mean convention [19], both the dispersive and non-dispersive components of the surface energy could be obtained. The result for *V* is shown in Figure 6. The γ_s^d follows a pattern roughly analogous to that shown by the IGC results, although the actual values are significantly lower than those obtained by the chromatographic method. This may be rationalized [20, 21] as showing that the Vectra surface has a broad distribution of dispersion site energies, the most energetic ones being sensed preferentially by the small number of molecular probes involved in IGC. The massive drop used in CA work would report on an average site energy for the entire surface. Arguably, with rising temperature the discrepancy between IGC and CA results should diminish, thereby accounting for the evident differences in the slopes of

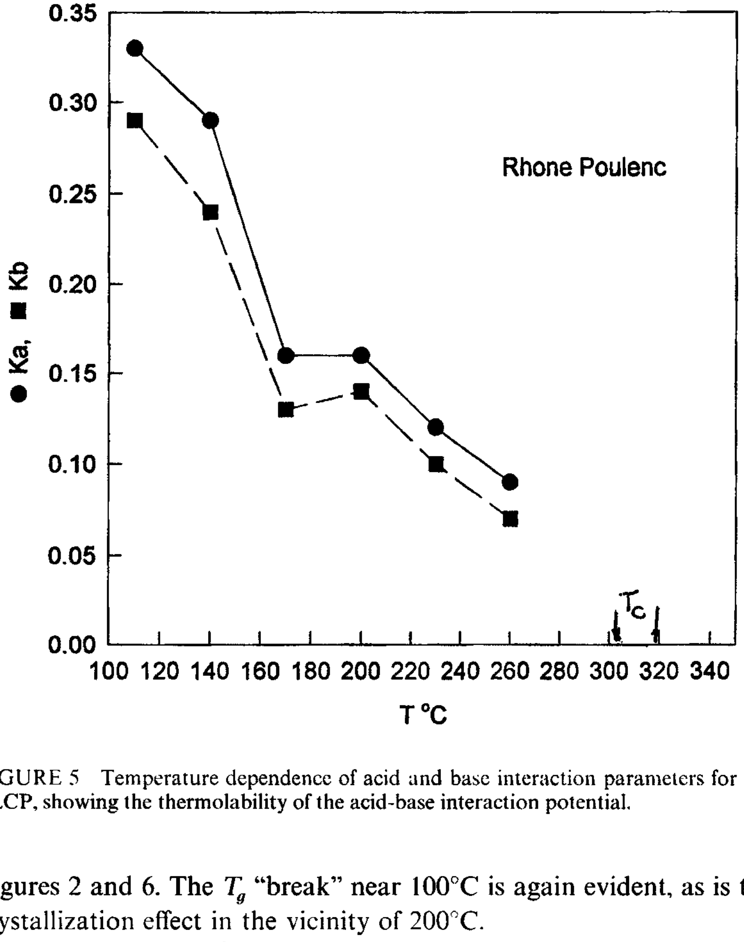

FIGURE 5 Temperature dependence of acid and base interaction parameters for RP TLCP, showing the thermolability of the acid-base interaction potential.

Figures 2 and 6. The T_g "break" near 100°C is again evident, as is the crystallization effect in the vicinity of 200°C.

The behavior of γ_s^{nd} is of particular interest. Below T_g the value (6–7 mJ/m^2) seems low for a polymer whose structure includes groups of substantial polarity. The reason may lie in the preferential orientation of the polar moieties into the bulk of the polymer. Indeed, it may be this strong orientational tendency of the TLCP that leads to the self-assembly characteristics of the polymer. This argument is supported strongly by the large increase in γ^{nd} as the glass transition interval is traversed. The increased chain mobility may lead to greater accumulation of polar moieties in the surface region of the TLCP. The increase to about 15 mJ/m^2 may then be taken as a measure of the difference in composition between surface and bulk regions of the

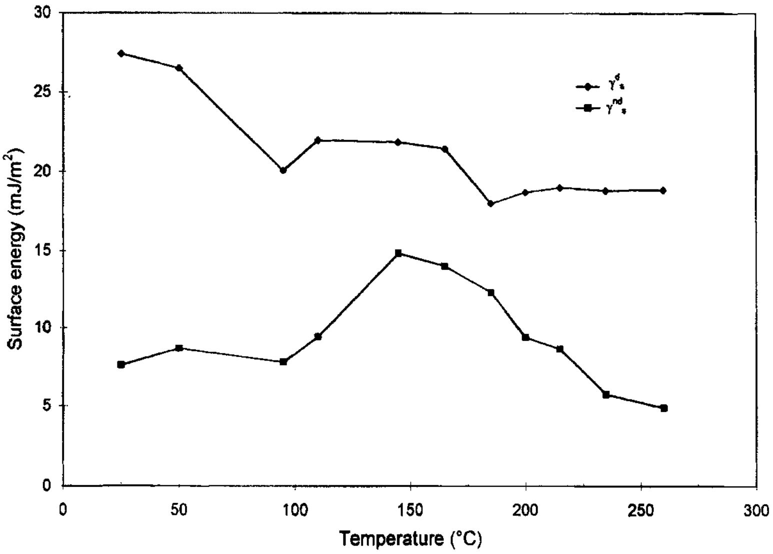

FIGURE 6 Apparent temperature variation of dispersive and non-dispersive surface free energies for Vectra TLCP, determined from contact angle data.

polymer. The preferential orientation of the higher energy, polar moieties into the polymer bulk may be assumed to originate with the thermodynamic demands for surface energy minimization. This demand is increasingly met as the conditioning temperature rises above 150°C, with polar groups now strongly oriented into the polymer bulk, leading to a marked decrease in the measured γ_s^{nd}. Assuming the established trend in this relation to continue, the abscissa would be cut at a T_c value not greatly different from that defined for the TLCP by the acid-base interaction parameters in Figure 4, again indicating that only dispersion forces remain active at the polymer surface.

iii. Various factors, such as large differences between the viscosities of constituent polymers, contribute to the limited miscibility displayed in many TLCP-thermoplastic blends. The present work raises the possibility that the immiscibility attributed to such blends is due, at least in part, to the inability of the self-assembled TLCP to exert adequate specific interactions at interfaces with polar polymers of the PC and PI type. However, if the acid-base interaction potential weakens at high temperatures, as suggested, then at temperatures above the critical for the persistence of acid-base functionalities, longer range dispersion forces should be predominant at interfaces of a TLCP/thermoplastic pair. These should be much more favorable for the establishment of miscibility, particularly if the host polymer also is above its characteristic temperature for the cessation of acid-base interactions. In the case of Vectra, then, blends with PC and PI should be immiscible when prepared below about 300°C, but should appear to be increasingly miscible if prepared at, and quenched rapidly from, temperatures $\geqslant 320$°C. SEM analyses of blends prepared at 280 and 320°C may be called upon to judge the issue.

Shown in Figure 7 are results for blends of PI/V at 15 wt% of the TLCP. There is little evidence of interconnection between host and TLCP in Figure 7A, relating to the blend made at 280°C. The blend prepared at 320°C, however, has a distinct morphology, with significant evidence for matrix/additive bridging, as seen in Figure 7B. The situation in PC blends is fully analogous, as illustrated in Figures 8A and B. These show the morphology of PC/RP blends at 20 wt% of the

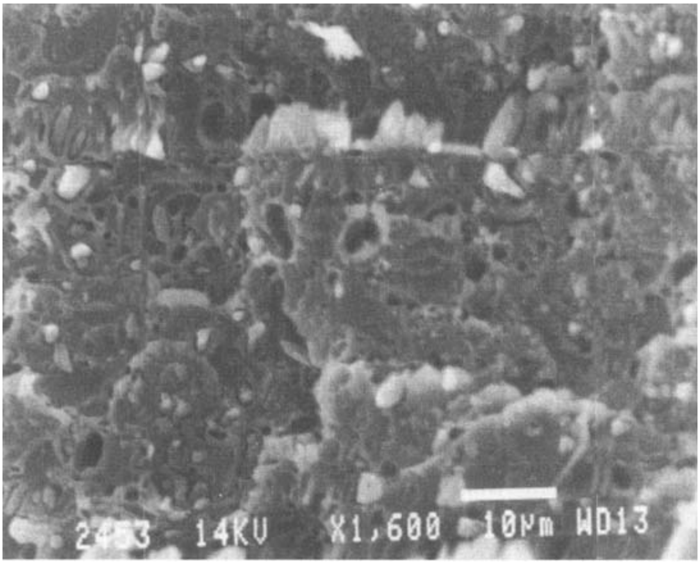

FIGURE 7A SEM of PI/Vectra blend (15 wt% TLCP), prepared at 280°C.

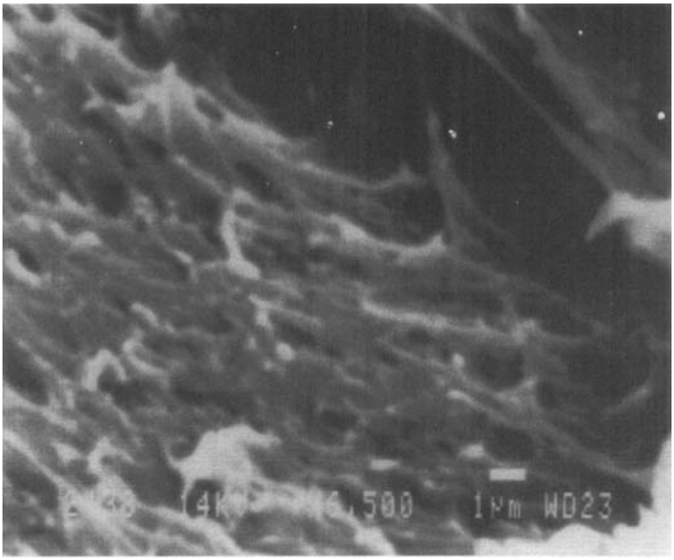

FIGURE 7B SEM of same blend prepared at 320°C.

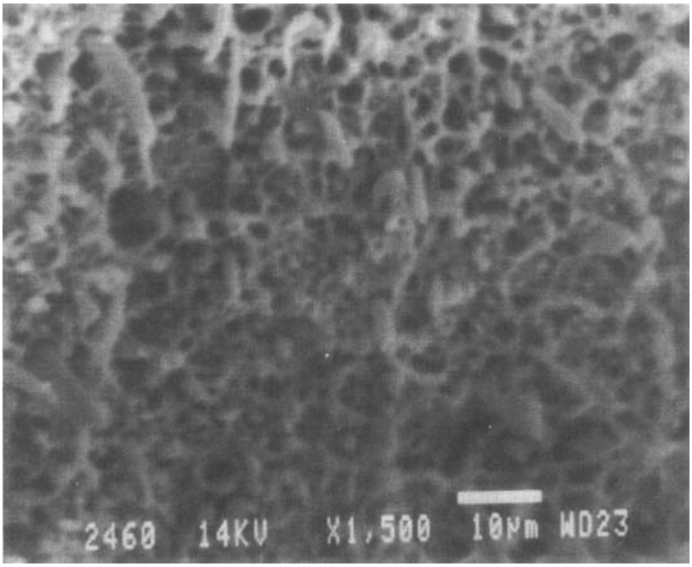

FIGURE 8A SEM of PC/RP blend (20 wt% TLCP) prepared at 280°C.

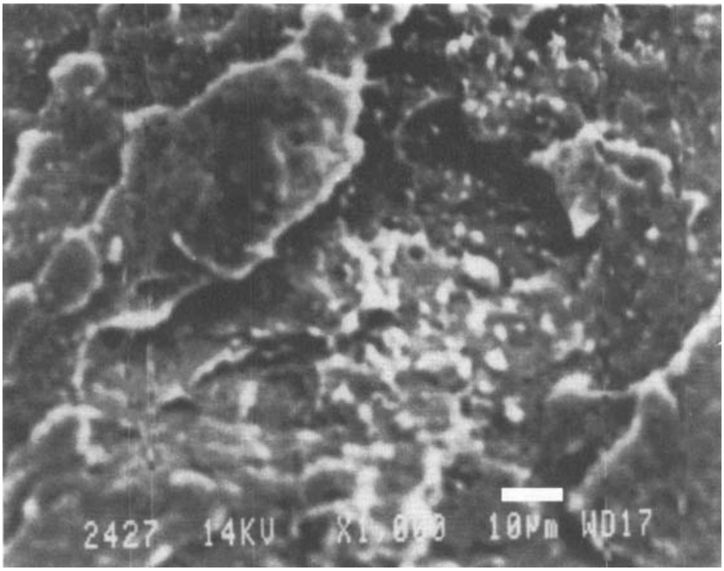

FIGURE 8B SEM of same blend prepared at 320°C.

TLCP. As before, the 280°C blend (Fig. 8A) has the typical structure of an immiscible system. In contrast, the connectivity between TLCP and matrix shown in Figure 8B for the blend made at 320°C is consistent with much increased component miscibility. These findings are analogous and in agreement with those reported by Kim and Denn [22] and Tang and coworkers [23]. The former extruded blends of polyethylene terephthalate and Vectra at T in the 275–285°C range, and found no SEM evidence for bridging between the polymers. However, on annealing at 310°C, substantial connectivity between the polymer phases was established. DSC and NMR [23] data also suggested an enhancement of miscibility in the course of annealing at the elevated temperature. Of course, it follows that the miscibility of blends prepared at 320°C is unstable, and at temperatures significantly lower than about 310°C, a reversion to the phase-separated morphology should take place. At room temperatures, well below the T_g of the polymers, the reversion would be very slow. Additional information is being gathered on the reality of the immiscibility/miscibility transition, on the thermolability of the acid/base functionality in

TLCPs, and on consequences of these phenomena on properties of polymer blends and composites.

CONCLUSION

- IGC and contract angle data indicate that in TLCP's here represented by Vectra and a Rhone-Poulenc polymer, substantial differences in composition exist between polymer surface and bulk.
- Strong tendency has been shown for polar moieties in TLCP to be oriented into the polymer bulk, possibly accounting, in part, for the self-assembly characteristics of these polymers.
- The polar, or acid-base, interaction potential of the present TLCP is thermolabile, and appears effectively to disappear above about 300–320°C.
- Blends of the TLCP with polycarbonate and a polyetherimide display very different morphologies when prepared at temperatures above and below the range associated with the elimination of acid-base forces in the TLCP. When prepared below that temperature interval, the blends appear as typical immiscible mixtures. When blended at 320°C, there is significant linkage between TLCP and matrix, suggestive of increased miscibility.

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