

Evidence of Chemical Reaction in Binary Blends of Polycarbonate and a Semi-Flexible Liquid Crystal Polymer

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Abstract: In this study, we provide the experimental results of the binary blends of a semi-flexible nematic liquid crystal polymer (LCP1) and polycarbonate (PC) within their phase diagram. The LCP1/PC blends were investigated by Differential Scanning Calorimetry (DSC), Optical Microscopy (OM), Wide-angle X-Ray Diffraction (WXRD), Fourier Transfer Infrared (FTIR), Gel Permeation Chromatography (GPC), and Nuclear Magnetic Resonance (NMR) techniques and observed the evidence of chemical reaction between LCP1 and PC in their heat-treated blends possibly by transesterification mechanism.

Keywords: Liquid crystal polymer, polycarbonate, binary blend, chemical reaction, transesterification.

1. INTRODUCTION

Liquid Crystal Polymers (LCP) exhibit a highly ordered structure in both the melt and solid states. It can replace such materials as ceramics, metals, composites, and other plastics because of its outstanding strength at extreme temperatures and resistance to virtually all chemicals, weathering, radiation, and burning. LCPs have high melt flow and fast setup which allow them to be molded into large, heavy-walled parts as well as thin-walled components [1-4].

The composite materials with LCP for use in engineering applications should satisfy the following requirements: (i) to consist of at least two physically distinct and mechanically separable materials called *matrix* and *reinforcing component*; (ii) to prepare by admixing of the above components and (iii) the composite to possess several properties being superior to that of the individual components [5].

Among the three basic groups of *macro-composites*, *nano-composites* and *molecular-composites* the LCP-containing composites can be considered the closest example of molecular composites. Under their molecular structure and conformation, the LCPs tend to form *in situ*, during processing, with very fine fibers having similar or better reinforcing efficiency as compared to that of conventional inorganic fibers [6].

A substantial amount of work has been performed in the area of LCP composites. They possess some important advantages over the conventional fiber-reinforced systems: single-step formation, e.g. during the injection molding of the part; improved mechanical integrity of the material; and very good mechanical properties. The inherently high strength and stiffness of the LCPs not only improve the mechanical properties of the resulting blend, but the processing is also free from problems associated with conventional short-fiber composites such as fiber breakage, wear of the equipment, and increase in viscosity [7-10].

Although the basic structural and self-reinforcing criteria of LCPs have been well developed, the optimization of blending and processing conditions to achieve desirable mechanical and rheological properties of their composites with commercial thermoplastics (TP) is still an open field of research. The partial crystalline state of LCPs imparts these plastics with many unique properties such as toughness, exceptional strength, chemical resistance, and high temperature. In addition, the two melting points of thermotropic nematic LCPs offer a broader processing range for these unique polymers. Over the years, based on new potential applications in other fields, such as actuators, organic photovoltaic, renewable energy, and new macromolecular architectures [11-15], a marked shift in the development of new LCPs has been noticed.

Whereas the technology and engineering of LCP-reinforced thermoplastics (TP) have been rather well developed, the knowledge of structure-property relations for optimization of processing and prediction of the mechanical properties of LCP/TP composites are

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still far from being complete. The available literature on the mechanical mixing of binary LCP blends with aliphatic-aromatic and wholly aromatic moieties has shown either a matrix compatibility [16-19] or complete immiscibility and phase separation of the components [20-21].

While many macroscopic properties of LCPs are extremely advantageous, thermoplastic polymer blends with LCPs have also been studied extensively as processing aids and reinforcement. There has been a rich literature on the blends of rigid LCPs, such as Vectra-A, Vectra-B, Xydar, and X7G, with commercial thermoplastics including polycarbonate (PC), polystyrene (PS), polyvinyl chloride (PVC), polyethylene (PE), poly-tetra-fluoro-ethylene (PTFE) and polypropylene (PP), which distinguish themselves from standard thermoplastics because of their better flow state during processing. Because of growing interests in applications of LCPs as a processing aid and reinforcement of engineering plastics, the need for the prediction of properties and mechanical behaviour of these high-performance composites has entered a new phase of research and development.

However, it has been shown that the miscibility of LCP blends is a major obstacle in their applications, and introducing some kind of interaction between LCP and flexible-coil polymers have been necessary to improve the miscibility of the two polymers. In this respect, the choice of LCP's chemical structure in blends with flexible chain thermoplastic polymers has been shown to involve chemical reactions. [22-26] Consequently, the thermotropic LCPs with flexible spacers and relatively low melting temperatures could provide some advantages compared to rigid LCPs, such as lower processing temperatures and better compatibility with flexible thermoplastics.

Concerning LCP blends with PC, there exist some scientific literature including studies on various rigid and semi-rigid LCP additives, compatibilizers, and processing aids [27-44], exhibiting chemical reactions, including transesterification [45-49]. In addition, other studies indicated that amorphous PC can be induced to crystallization by the synergistic action of LCP reactive compatibilizer [47], and transesterification in in-situ PC/aromatic-LCP blends exhibited increased compatibility consistent with improvements in mechanical property parameters of the blends [48]. However, by minimizing transesterification in PC/flexible-LCP blends, the tensile modulus of the blend was improved [49].

In the present study, to confirm the occurrence of chemical interaction in LCP and thermoplastic composites for industrial application, we utilized six various characterization techniques (DSC, OM, WXRD, GPC, FTIR, and NMR) and studied the heat-treated blends of a low molecular weight semi-flexible liquid crystal polymer (LCP1) with commercial polycarbonate (PC) at various concentrations. The experimental results of heat-treated blends with all techniques confirmed the miscibility of the two incompatible polymers due to chemical reactions.

2. EXPERIMENTAL

2.1. Materials

The Polycarbonate (PC) material was Sinvet-301 (EniChem) with a glass transition of $T_g = 154\text{ }^{\circ}\text{C}$ and was used as received. The LCP material was a semi-flexible nematic liquid crystal co-polyester referred to as SBH1 in the previous works [50-53] and it is codified as LCP1 in this study.

The semi-flexible co-polyester LCP1 was synthesized by melt poly-condensation of mixtures of *4,4'-di acetoxy biphenyl* (DBP), *sebacic acid* (SA), and *4-acetoxybenzoic acid* (HBA), resulting in the synthesis of copolymer LCP1 with the following chemical structures and compositions:

$\text{-}(\text{-O-C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{-})\text{-}(DBP)$	$\text{-}(\text{-OC-(CH}_2)_8-\text{CO-})\text{-}(SA)$	$\text{-}(\text{-O-C}_6\text{H}_4-\text{CO-})\text{-}(HBA)$
25%	25%	50%

The crystal-nematic transition (T_{KN}) of LCP1 was $221\text{ }^{\circ}\text{C}$ and its nematic-isotropic (T_{NI}) transition was estimated to be above $400\text{ }^{\circ}\text{C}$ and could not be properly determined due to decomposition of LCP1 at around $350\text{ }^{\circ}\text{C}$. The LCP1/PC blends were made by direct mixing of the powders of the two components. The mixing and heat treatment of the blends were performed in Brabender with 10/90, 25/75, 50/50, and 70/30 LCP1/PC weight ratios below ($215\text{ }^{\circ}\text{C}$) and above ($257\text{ }^{\circ}\text{C}$) the T_{KN} of LCP1 followed by direct heat cycling in the DSC pans within $50\text{--}300\text{ }^{\circ}\text{C}$ temperature range until there was no change in the transition temperatures.

2.2. Methods

We utilized various characterization methods, including Differential Scanning Calorimetry (DSC), Optical Microscopy (OM), Wide-Angle X-Ray Diffraction

(WXRD)), Gel Permeation Chromatography (GPC), Fourier Transfer Infra-Red (FTIR), and Nuclear Magnetic Resonance (NMR) spectroscopy in the study of LCP1/PC blends. The detailed descriptions of these methods and techniques are as follows

The DSC method was utilized to measure the transition temperatures and T_{KN} transition enthalpies of pure materials and their binary blends. The DSC measurements were carried out on 10-20 mg samples utilizing a Perkin-Elmer DSC-7 instrument at a heating rate of 20°C/min rate. The binary LCP blends were carried out in a DSC pan by direct weighing and mixing of the components and through repeated heating and cooling cycles (usually 3-4 times) until no further changes were observed in the transition temperatures of the blends.

The OM measurements by a Leitz-Wetzaler polarizing microscope equipped with a Linkam THM600 hot-stage and TMS90 temperature control units were utilized to determine the texture of the materials. After the completion of DSC measurements, the same mixtures were used to determine the transition temperatures with the OM method. All OM in heating and cooling modes of 5-80 °C/min rates under a nitrogen atmosphere.

The WXRD studies of the powder samples were performed by a wide-angle Philips X-Ray Powder Goniometer. All XRD spectra were obtained at room temperature during 2-3 hours of exposure with a Cu-K α radiation source.

The Waters Associates GPC instrument was utilized to determine the molecular weights of PC and LCP1/PC blends. The semi-quantitative measurements of the samples at a concentration of 0.2% (w/v) in THF were carried out using a tetrahydrofuran (THF) mobile phase with UV-254 nm light detector.

The FTIR spectra were obtained using a Perkin-Elmer 1760 spectrometer and the measurements were carried out on both films and powders of single component and blends where all data analysis were accomplished after 9 spectra scans.

The NMR spectroscopy of the samples solutions in chloroform was performed by a Bruker AC-200 spectrometer using TMS as an internal reference. For each sample, both ^1H and ^{13}C spectra were obtained. In the case of LCP1, which is not soluble in chloroform, the NMR measurement was carried out in pentafluoro

phenol (PFP) solution on a Bruker CXP-300 spectrometer.

3. RESULTS & DISCUSSION

The experimental results presented in this study mainly focus on the qualitative presentation of a chemical reaction between LCP1 and PC in their blends. Further in-depth understanding of the specific nature and type of such molecular interactions depends on some Physico-chemical conditions that require a further systematic investigation, which is beyond the context of the present study.

3.1. DSC Results

Based on DSC calorimetric method, we measured the transition temperatures and enthalpies of pure LCP1, PC, and their blends LCP1/PC at 10/90, 25/75, 50/50, 75/25 (w/w %) concentrations. The glass (T_g) and crystal-nematic (T_{KN}) transition temperatures of the phase diagram of LCP1/PC blends are presented in Figure 1. The blends were prepared in a DSC pan by direct weighing of the components and the complete mixing was obtained after 3-4 heating-cooling cycles where no further change in their DSC thermograms was obtained.

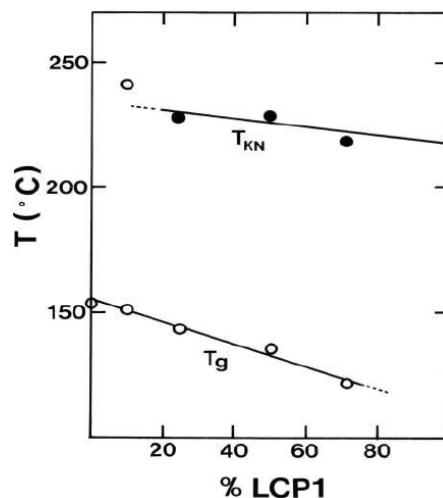


Figure 1: The phase diagram of LCP1/PC blends showing the T_{KN} and T_g transition temperatures obtained by the DSC method.

Examples of DSC thermograms of pure components and three LCP1/PC blends are shown in Figure 2, where we found that below the 20% of LCP1 composition, the blends consist of the primarily one-phase region, where the two polymers were completely miscible or interactive. This effect is due to the disappearance of the T_{KN} transition of LCP1.

Above the 20% LCP1 composition, the blends exhibited two-phase regions, exhibiting the individual T_g and T_{KN} transitions of PC and LCP1, respectively. Also according to Figure 2, by increasing the LCP1 composition in the blend the excess amount of LCP1 becomes evident by the increase of the peak intensity of T_{KN} transition.

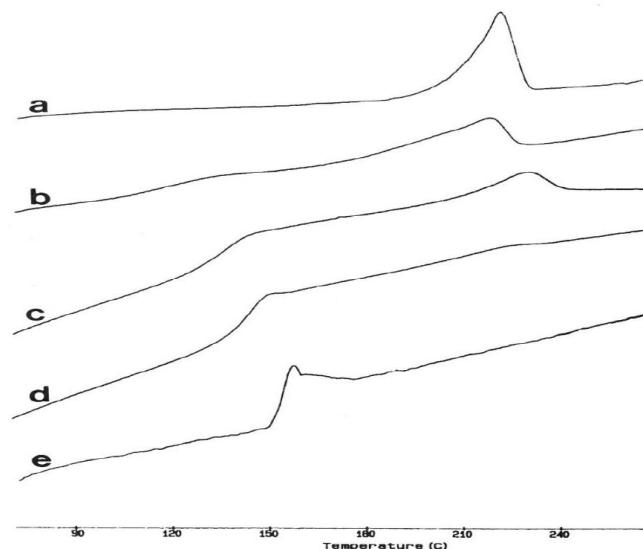


Figure 2: The DSC thermograms of **a**) pure LCP1, and LCP1/PC blends at **b**) 25/75, **c**) 50/50 and **d**) 75/25 weight ratios, and **e**) pure PC at 20 deg/min heating rate.

This is also evident in the phase diagram of Figure 3, that by increasing the T_{KN} transition enthalpy (ΔH_{KN}) of LCP1 as a function of its composition, which manifests the contribution of the crystalline structure of LCP1 into the blends. In addition to the behavior of the thermal transition in the phase diagram (Figure 2), there are two other observations that deserve an explanation. The first observation is the linear decrease T_g of PC by increasing the LCP1 composition, which according to the miscibility rule can occur only if LCP1 has also a T_g below that of PC.

Although we have not observed a T_g transition for LCP1, the possibility that its glass transition is below that of PC could not be ruled out. In the phase diagram of Figure 1, one could deduce a $T_g = 60$ °C for LCP1 by a simple extrapolation to pure LCP1. A similar rationale for T_g of LCP1 could be also explained by the molecular weight reduction of PC due to chemical reaction with LCP1. We observed a reduction in the molecular weight of the PC-enriched phase by GPC technique, which will be discussed later in the corresponding section.

The occurrence of chemical reaction in LCP1/PC blends, probably by transesterification mechanism, is

evident by the increase in T_{KN} transition of LCP1 by reduction of its content in the phase diagram (Figure 1). This effect, which is in contrast to the partial miscibility concept, could be a result of an increase in the molecular weight of the LCP1-enriched phase or due to its subsequent interaction with PC.

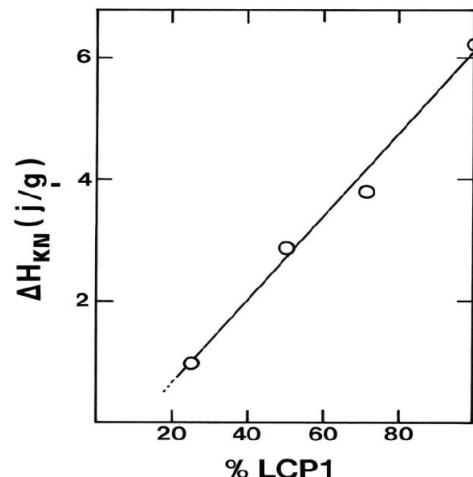


Figure 3: The crystal-nematic (T_{KN}) transition enthalpies of LCP1/PC blends as a function of LCP1 composition. At above the 20% LCP1 composition, the T_{KN} transition was not observed.

A further indication of chemical interactions between LCP1 and PC is achieved by heat treatment of the blends by preparing 4.0 grams of 50/50 mechanical mixture of LCP1 and PC components and heating in the vacuum oven at 250 °C for 6 hours. The blended sample was then dissolved in CH_2Cl_2 solvent and refluxed with the Kumagawa method for around 10 hours at 40 °C. The weight of recovered insoluble residue was 1.7 grams and that of the soluble portion was 2.3 grams. This indicated that around 29% of LCP1 has remained in the solution and 21% remained in the residue. In Figure 4 we present the DSC thermograms of the blend after heat treatment (Figure 4a), CH_2Cl_2 soluble portion (Figure 4b), and CH_2Cl_2 insoluble residue (Figure 4c). The heat-treated blend exhibits a *decrease* in T_g of PC from 154°C to 138°C and an *increase* of T_{KN} of LCP1 from 221°C to 241°C. The soluble part (Figure 4b), which consisted mainly of PC, showed a further reduction of T_g to 132°C, whereas the LCP1 residue (Figure 4c) exhibited a single T_{KN} at 241°C.

The DSC results of the heat-treated LCP1/PC blend by itself indicate the apparent miscibility of the blend is due to chemical interaction and its degree depends on the temperature and time of heat treatment. Note that based on differences in their chemical structures, it is

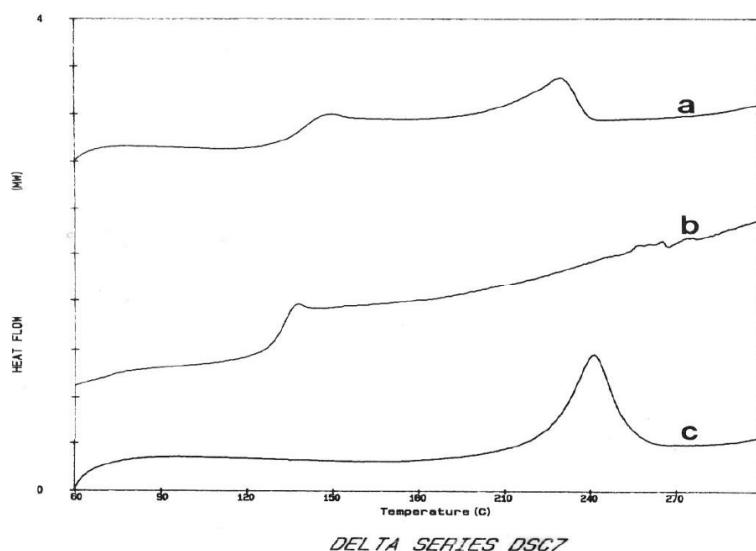


Figure 4: DSC thermograms of 50/50 LCP1/PC blend **a)** after heat treatment, **b)** soluble portion in CH_2Cl_2 and **c)** insoluble portion in CH_2Cl_2 , at 20 deg/min heating rate.

not expected that PC and LCP1 be miscible in the first place. As we will see in the following sections, the reaction between the two polymers leads to a significant decrease in the molecular weight of PC and the formation of chemical bonds between PC and the remaining fractioned LCP1 molecules.

3.2. OM Results

All the studied blend samples with DSC were also subjected to OM analysis. Although not presented here, the OM results, in agreement with DSC measurements, confirmed the formation of complete compatibility of up to around 20% LCP1 content and a two-phase region at higher LCP1 compositions. The two-phase regime consisted of a PC-enriched glass phase and an LCP1-enriched crystalline structure. Above T_g , the glass phase melted to an amorphous

state and above T_{KN} the crystal structure melted to a nematic phase.

In addition to these obvious textural behaviors, we found that below T_g , both heat-treated PC-enriched and LCP1-enriched blends exhibit birefringent glassy textures. Examples of these glass textures are shown in the micrographs of Figure 5, which indicate that the birefringence is due to the inherent birefringence of the LCP1 matrix.

3.3. WXRD Results

In agreement with DSC and OM methods, the WXRD studies of LCP1/PC blends were not only in favor of compatibility but also were in accord with the possibility of chemical interaction between PC and LCP1 components. In Figure 6, we present the WXRD

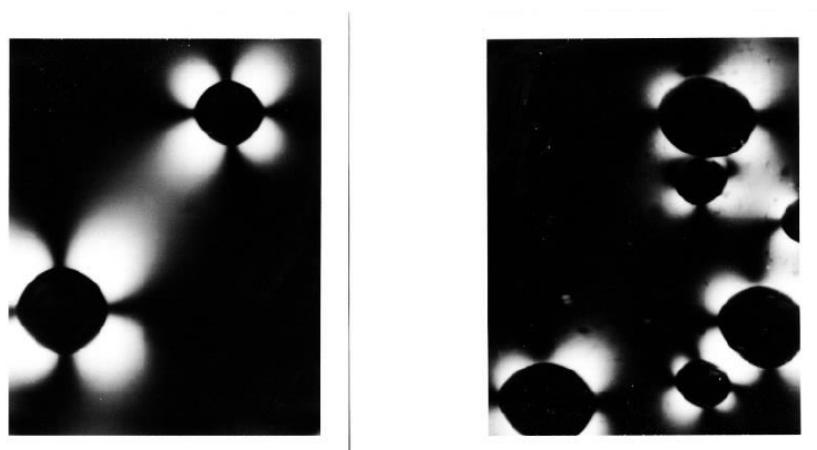


Figure 5: The OM micrographs of birefringent phases of (left) PC-enriched and (right) LCP1-enriched blends under crossed polarization at room temperature.

spectra of a heat-treated LC1/PC (10/90) blend as a function of treatment time. Figure 6a is from the original pressed powder blend exhibiting a broad reflection of amorphous PC (centered at $2\theta = 17.0$ deg) and a reflection of crystalline LCP1 (centered at $2\theta = 20.5$ deg).

The diffraction pattern of this sample after subsequent heat treatments at 260 °C after 2, 5, and 15 minutes are presented in Figures 6b-d, respectively. The results indicate a gradual decrease (6b-c) and disappearance (6d) of LCP1 crystal diffraction after heat treatment. Referring to Figure 6, it should be noted that, the disappearance of LCP1 crystal reflection is accompanied by further broadening of the PC reflection spectrum. These two coupled effects point out more favorably to the occurrence of a chemical reaction than the miscibility of the LCP1 and PC. Because of the two polymers were miscible in the solid-state, one should expect to observe the sharpening of PC reflection. Consequently, according to WXRD data, the reduction and subsequent disappearance of crystal reflection of LCP1 in the heat-treated blend is not a result of the loss of its crystalline order through miscibility but is due to the chemical interaction between the two polymers under heat treatment.

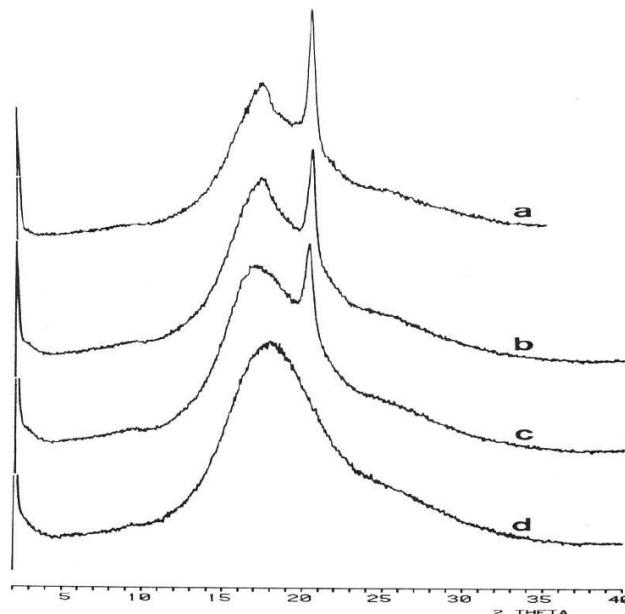


Figure 6: WXRD spectra of 10/90 LCP1/PC blend **a)** before heat-treatment and after heat-treatment in **b)** 2.0, **c)** 5.0 and **d)** 15 minutes at 260 °C under hot press.

3.4. GPC Results

The GPC chromatograms of LCP1/PC blends were studied to obtain semi-quantitative knowledge of the

number of species and the range of their molecular weight dispersion after heat treatment. In the present study, we only measured the relative molecular weight dispersion of a blend obtained from the soluble portion of a 90/10 LCP1/PC blend treated in a vacuum oven (see Figure 4b). The chromatogram of this sample was compared with that of pure PC to study the effect of heat treatment on the molecular weight of PC. Both pure PC and LCP1/PC blends were dissolved in THF at a low concentration of 0.2 w/v and separately injected in the GPC column. The mobile phase was THF and the retention time was calibrated against Toluene.

The results as presented in Figures 7a and 7b, respectively, indicate that the PC-enriched portion of the blend (Figure 7a) has a substantially lower molecular weight than pure PC (Figure 7b). We can deduce two criteria from the GPC data of Figure 7. Firstly, from the larger retention time of the blend ($t=35.8$ min) than that of PC ($t=34.2$ min) and secondly, from higher sensitivity of LCP1/PC blend concerning PC. Note that the peak sensitivity of blend is an indication of an increase in the number of end-chain functional groups, such as carboxyl and hydroxyl groups. The increase in the number of functional groups in the blend must be due to the reaction between the fractionated LCP1 and PC chains. It should be noted that until now, none of the utilized methods, including the FTIR and NMR that will be discussed later, indicate any evidence on the presence of fractionated LCP1 molecules as free species in the blends.

Conclusively, in agreement with DSC and WXRD studies, and as it will be supported by FTIR and NMR studies in the following sections, the GPC results also indicate that, due to chemical interaction, the molecular weight of PC is decreased during the heat treatment of the blends and contained some LCP1 moieties in its structure as a one-component species.

3.5. FTIR Results

The initial studies of LCP1/PC blends by FTIR technique also favor the existence of LCP1 bounded moieties by heat treatment. Despite the complexity of the FTIR vibrational spectra of these polymers, we only focus on the major vibrations which are useful in this verification. In Figures 8a and 8b, we present the FTIR spectra of PC and LCP1 within the 400-4000 cm^{-1} range, respectively.

The spectrum of PC was obtained from a film whereas that of LCP1 was taken from powder in a KBr

cell. The vibrational bands of interest in the PC spectrum (Figure 8a) consisted of the -CH₃ stretching bands at 2968, 2936, and 2973 cm⁻¹; the C=O singlet at 1775 cm⁻¹, the doublets at 1603 and 1594 cm⁻¹, as well as two other unidentified singlets at 1015 and 1080 cm⁻¹. The vibrational bands of interest in LCP1 spectrum (Figure 8b) were the broad hydroxyl group at 3457 cm⁻¹; the symmetric and asymmetric -CH₂ stretching bands at 2853 and 2930 cm⁻¹; the aromatic =C=O stretching at 1756 cm⁻¹; the aliphatic =C=O vibrations at 1735 and 1740 cm⁻¹ and the three unidentified singlets at 1005, 1052 and 1600 cm⁻¹.

Considering the differences between these selected vibrations of PC and LCP1, in Figure 9a and 9b we

plotted the FTIR spectra of the soluble portions of two heat-treated LCP1/PC blends at 90/10 (Figure 9a) and 50/50 (Figure 9b) weight ratios, respectively. It should be noted that after heat treatments, the 90/10 blend was soluble in CH₂Cl₂, whereas the 50/50 blend provided a soluble portion and an insoluble residue consisting of around 80% of the original LCP1.

In addition to the obvious vibrations of PC, The FTIR spectra of the blends also clearly exhibit the vibrational bands of LCP1 moieties. As supported by the results of GPC and NMR (see the next section), the existence of LCP1 vibrations in these one-component samples is additional strong support for chemical bindings between PC and LCP1 components.

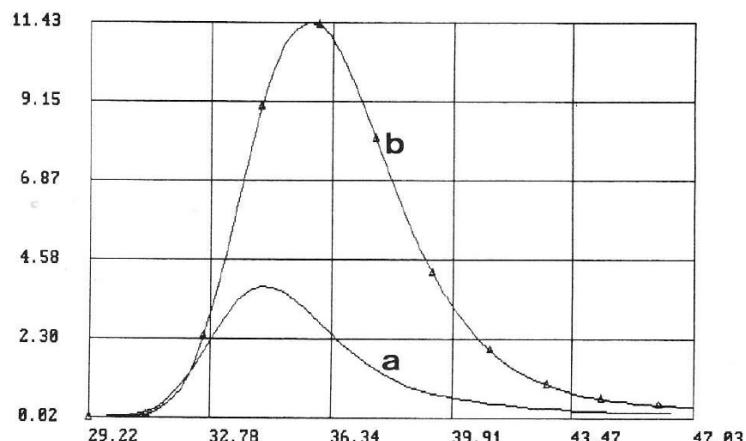


Figure 7: The GPC chromatogram in THF at 254 nm of a) pure PC and b) 10/90 LCP1/PC blend. The vertical axis is in the arbitrary unit and the horizontal axis is the retention time in minutes.

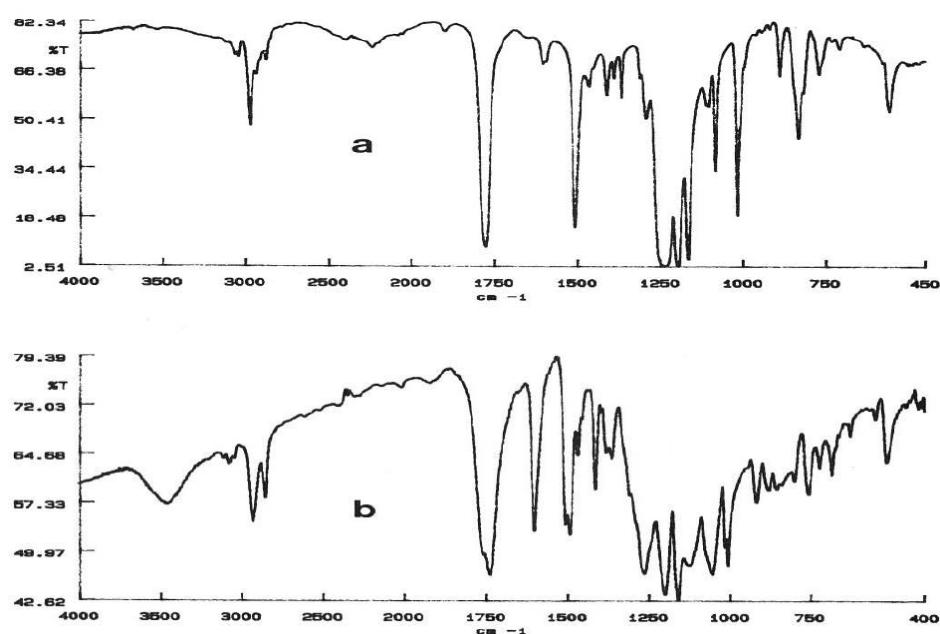


Figure 8: The room temperature absorption FTIR spectra of a) PC film and b) LCP1 powder within 400-4000 cm⁻¹ range.

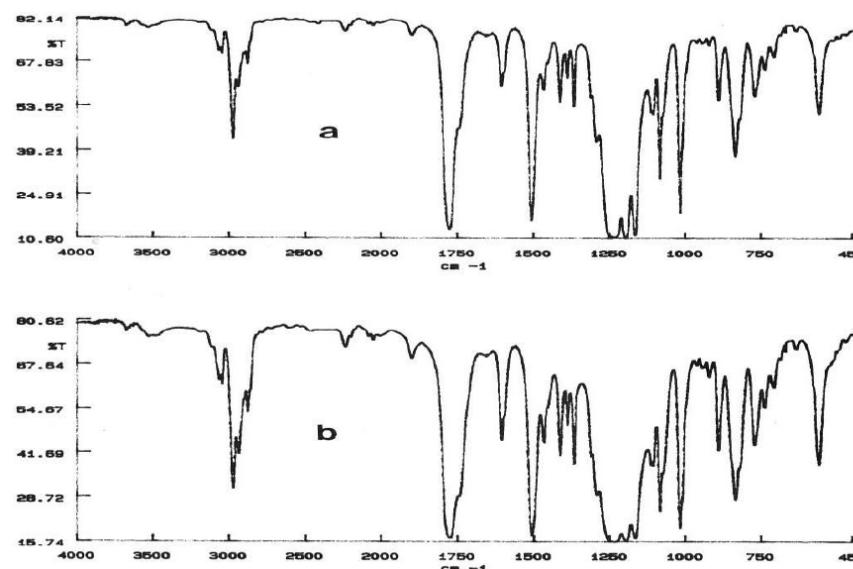


Figure 9: The room temperature absorption FTIR spectra of soluble portions of a) 10/90 and b) 50/50 LCP1/PC blends within 400-4000 cm⁻¹ range.

Subsequently, according to Figure 9, the existence of LCP1 in LCP1/PC blends could be found in the following vibrations:

- Presence of hydroxyl vibration at 3450 cm⁻¹,
- Relative intensities of 2857 and 2932 cm⁻¹ shoulder vibrations,
- Existence of aliphatic =C=O vibration at 1745 as a shoulder,
- Increase in relative intensity of 1603 cm⁻¹ vibration compared to pure PC.
- The appearance of two shoulder signals at 1008 and 1071 cm⁻¹.

Without further analysis of the FTIR spectra, these qualitative results are a sufficient indication of the presence of LCP1 species in the chemical structure of PC. Note that, the reported FTIR studies of heat-treated blends are similar to those presented in Figure 9. However, by different heat treatments, the assigned vibrational bands could show various intensities as a result of different degrees of chemical interactions.

3.6. NMR Results

The pure PC and LCP1 materials and their blends were subjected to both ¹H and ¹³C NMR analysis. In Figures 10a and 10b, we provide the ¹H NMR spectra of PC and a soluble portion of 50/50 heat-treated LCP1/PC blend, respectively. The spectra of samples

were obtained from their solutions in chloroform and TMS was used as an internal standard.

The peak assignments of PC spectrum (Figure 10a) in a strait forward, where the -CH₃ protons show a singlet at 1.7 ppm and the aromatic protons exhibit quartet centered at 7.2 ppm. In addition to these signals, in the spectrum of LCP1/PC blend (Figure 10b) also consists of other following minor signals: Two triplets at 1.4 and 2.55 ppm of the proton resonances of aliphatic -CH₂ polymer chain; two doublets at 7.0 and 7.6 ppm are ¹H resonances of two types of dioxy-biphenylene protons and finally, a quartet centered at 8.3 ppm attributed to oxy-benzoate protons near to =C=O group. The presence of these small resonances is an indication of the presence of bonded LCP1 moiety in the chemical structure of PC structure after heat treatment.

A similar conclusion could be achieved from ¹³C NMR spectra of PC and LCP1/PC blends presented in Figures 11a and 11b, respectively. In comparison with ¹³C spectrum of PC (Figure 11a), the ¹³C spectrum of LCP1/PC blend (Figure 11b) consists of additional 13 satellite resonances at 25, 29, 35, 121, 129, 132, 138, 148, 151, 152, 155, 164 and 172 ppm. The only difference between these signals and those of LCP1 is their appearance at the higher end of the ¹³C spectrum. Note that, in the ¹³C spectrum of pure PC the =C=O moiety exhibits two doublet resonances at 168 and 178 ppm, instead are shifted to 164 and 172 ppm in the spectrum of LCP1/PC blend (see Figure 10b). Also, the absence of PC's =C=O resonance signal at 157 ppm in

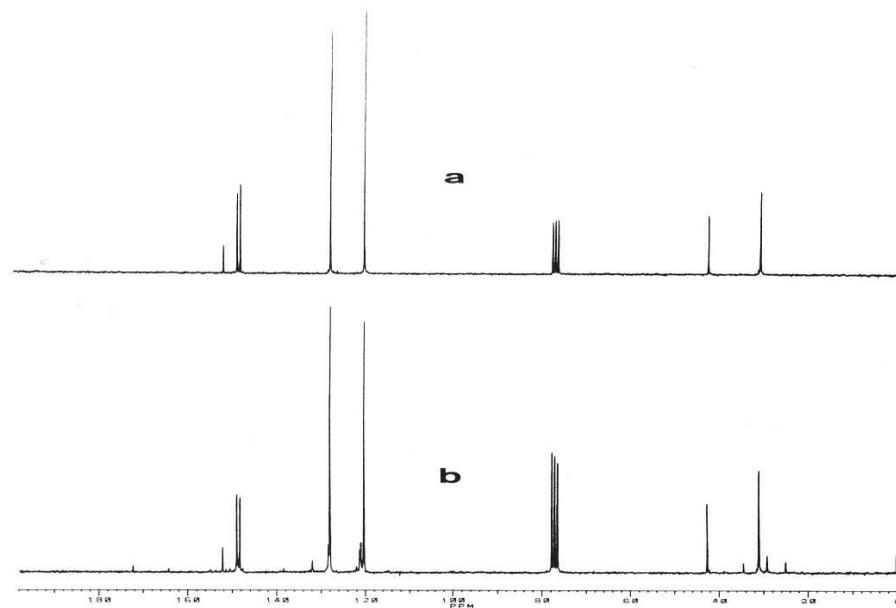


Figure 10: The ^1H NMR spectra of a) PC and b) 50/50 heat treated LCP1/PC blend in CDCl_3 at room temperature.

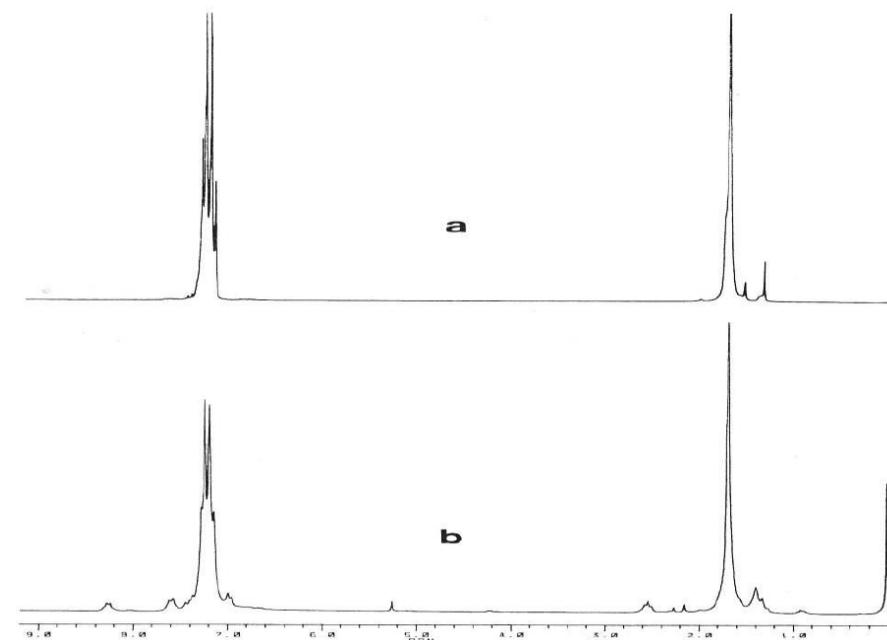


Figure 11: The ^{13}C NMR spectra of a) PC and b) heat-treated 50/50 LCP1/PC blend in CDCl_3 at room temperature.

the spectrum of LCP1/PC blend is further support of chemical reaction between PC and LCP1 components.

Therefore, in agreement with the results from other techniques, particularly with DSC, FTIR, and GPC results, we can also conclude that, during the heat-treatment of the blends, a definite molecular interaction takes place between PC and LCP1 polymer chains. In such interactions, which occur at above 20% LCP1, the chemical structure and macromolecular integrity of the original PC are preserved, but the molecular weight of

interacted LCP1 and PC species are smaller than that of the original PC.

Furthermore, although we do not have further information about the chemical structure of LCP1 in the blend, the present results suggest that its molecular structure has been drastically affected by heat treatment. Whatever the structural nature of the LCP1/PC blend may be, the present results indicate that it consists of one chemical species.

4. CONCLUSION

We reported on the binary phase diagrams of flexible nematic LCP1 and commercial PC thermoplastic blends. After heat treatment, the blends of these two initially incompatible polymers exhibit miscibility and evidence of chemical interactions between LCP1 and PC polymer structures in their heat-treated blends. The properties of heat-treated LCP1/PC blends studied with DSC, OM, WXRD, GPC, FTIR, and NMR techniques are significantly different from those of pure LCP1 and PC components, which strongly supports of the chemical interaction.

It is known that at high temperatures, polyesters can have chemical reactions with other polymers by either hydroxyl end-group reaction (*alcoholysis*), acid end-group reaction (*acidolysis*), or by the midchain ester-ester interchange (*transesterification*) [54,55]. It is also known that, in the case of high molecular weight polymers like LCP, due to low end-group concentration, the probability of chemical reaction by transesterification is much higher than alcoholysis or acidolysis reactions [56-59]. Hence, transesterification usually dominates the reaction process in relatively high molecular weight polyesters. As transesterification in such blends continues, new compatible amorphous blends will form and in LCP/thermoplastic blends, the liquid crystalline character of the blends is lost.

It has been reported that, in heat-treated blends of PC and random liquid crystal co-polyester, the ester-ester interchange in the two polymers takes place where the bisphenol-A unit of PC first reacts with terephthalate unit and then with an oxy-benzoate unit of liquid crystal co-polyester [27-30, 40], where the miscibility increases with transesterification in the blends of PC and other polyesters with LCPs. [56, 58-61]

Although in the present study of heat-treated LCP1/PC blends, the origin of a chemical reaction is likely transesterification, however, due to the lack of information on the molecular weights of the utilized LCP1 and PC, we hesitated to directly specify the transesterification and instead utilized the more general term *chemical reaction* throughout this study. Given the important nature of chemical reactions in LCP-reinforced thermoplastic composites with either mechanism, specifically for industrial applications, it will require further in-depth and systematic future investigations on LCP composites with commercial engineering plastics.

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DATA AVAILABILITY STATEMENT

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations.

CONFLICTS OF INTEREST

The author declares no conflict of interest. The internal funder had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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