Additive Effects on Thermotropic Liquid Crystal Polymer Alloys
I. Effects of Third Component of Thermotropic Liquid Crystal Polymer on Mechanical Properties of Vectra A-Reinforced Polycarbonate

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ABSTRACT: The effects of addition of the 3rd component of thermotropic liquid crystal polymer (TLCP) on the mechanical properties and structure of Vectra A-reinforced polycarbonate (PC) were studied. The 3rd TLCP was the copolymer of *p*-hydroxybenzoate (PHB) and ethyleneterephthalate, known as X-7G TLCP. PC, Vectra A, and a small amount of the 3rd TLCP were blended in the molten state, the extrudate of which was cut and injection-molded. The mechanical properties of the blends were improved dramatically by addition of a small amount of the 3rd TLCP component. SEM revealed that the blend systems were always phase-separated, even after injection-molded, and the fibrils of Vectra A in the injection-molded blends became finer and longer in the presence of the 3rd TLCP. FT-IR indicated that no special chemical reaction took place between the TLCP and PC. The dynamic viscoelastic analysis indicated that the addition of the 3rd TLCP component had almost no effect on the thermal endurance of the blends. X-Ray diffraction analysis showed that the orientation of Vectra A fibril in the blend became higher when the 3rd TLCP was added, which led to the great improvement of the mechanical properties. Based on the assumption of additivity law, the fibril modulus was evaluated and found to be in the same order as the orientation evaluation by X-ray diffraction. The thinning of fibrils by addition of the 3rd TLCP component was discussed based on the crystallization kinetics of rodlike molecules.

KEY WORDS   Polycarbonate / Liquid Crystal / Ternary Blends / Mechanical Properties / Morphology / Crystallization Kinetics /

As one of the applications of the thermotropic liquid crystal polymers (TLCP), the blends of engineering plastics and TLCP are promising the improvement of mechanical and thermal properties due to the reinforcing function and thermal endurance of TLCP. There have been many engineering and scientific reports on this subject. Kiss[1] suggested a concept of "*in situ composite*," emphasizing the fact that the TLCP reinforcement could be formed "*in situ*" during processing. Isayev *et al.*[2] called them as "self-reinforced melt processable polymer composite". According to Brostow *et al.*[3] the composite could be classified into two kinds: one was the traditional fiber-reinforced composite, being classified as a heterogenous composite; the other was the molecular composite, such as self-reinforced plastics and the molecular composite in the strict meaning suggested by Takayanagi.[4] From many papers reported on the blends of the engineering plastics and TLCP, one can find two important facts: such blend systems are usually phase-separated and

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their properties depend strongly on the processing conditions. To develop good fiber-reinforced polymer composites, a suitable adhesion between the fiber and the matrix resin is necessary. Similarly, in the TLCP/plastics system, the affinity between both components of the blend is important. As for the processing conditions, the reinforcing fibrils of TLCP in the blend orient under shear flow, resulting in a great influence on the mechanical properties.

Unfortunately, the blends of TLCP and the engineering plastics are usually phase-separated, especially when a wholly aromatic TLCP is used. Some papers reported to use the TLCP with long flexible spacer[5] or some special chain extenders[6] by which the chemical reaction between TLCP and plastics could take place to give an improved compatibility between both phases. Another report[7] suggested that when a semi-aromatic TLCP, typically the copolymer of poly(ethylene terephthalate) (PET) and poly(hydroxybenzoic acid) (PHB), known as X-7G of Eastman Kodak Co. was used, the flexible segment in the X-7G chain showed an affinity to the linear polyester such as PET, PBT, and PC, resulting in partial compatibility. But the thermal and mechanical properties of X-7G are lower than those of wholly aromatic TLCP, such as Vectra of Hoechst-Celanese Company and Xydar of Carborundum Company. Many papers[8-17]

reported on the modulus and strength of the PC/TLCP binary blend, which were not so good, judging from the criteria given in the later part of this paper. In this paper, we combined the advantages of both X-7G and Vectra A and blended them with the matrix resin of polycarbonate, forming a ternary blend system. In place of X-7G of Eastman Kodak Co. used in the above foreign papers, we employed here Rodlan of Unitika Co. as X-7G and Rodlan have essentially almost the same molecular structure. Reduced interfacial energy and rise of the orientation of TLCP fibril by addition of the 3rd component of TLCP were expected to improve the mechanical properties of the existing binary blends.

EXPERIMENTAL

Materials

Polycarbonate (PC) was supplied from Sumitomo Chemical Co. Wholly aromatic TLCP (Vectra A 950, VA) based on p-hydroxybenzoic acid (PHB) and 2,6-hydroxynaphthoic acid (HNA) was supplied by Polyplastics Co: in Japan. Two kinds of semi-aromatic TLCP based on the copolymer of PET and PHB (Rodlan LC-3000 and Rodlan LC-5000) were supplied by Unitika Co. in Japan. Table I lists the characteristics of these materials. The TLCP catalogue distributed

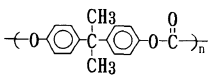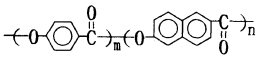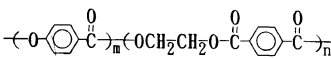**Table I.** Characteristics of polymers used in this paper

Materials: (Symbol) (Supplier)	Molecular structure	T_g °C	T_m °C
Polycarbonate: (PC) (Sumitomo Chem. Co.)	[chemical structure]	150	—
Vectra-A 950: (VA) (Polyplastics Co.)	[chemical structure]	—	274
Rodlan LC-3000: (R3) (Unitika Co.)	[chemical structure]	70	193
Rodlan LC-5000: (R5) (Unitika Co.)		70	202

Table II. Processing conditions

Extrusion		Injection	
Rotor temp	Spin die temp	Cylinder temp	Molder temp
°C	°C	°C	°C
250	310	310	100

from Unitika Co. noted that the content of PHB unit in Rodlan is 60% for Rodlan LC-3000 (R3) and 80% for Rodrun LC-5000 (R5).

Preparation of Blends

All the materials were dried in a vacuum oven at 100°C for at least 24 hours. The blends were prapared by using a Mini Max Polymer Evaluation System of Custom Scientific Instrument Inc. Blended samples were prepared by shear blending followed by extrusion. The bar specimens for tensile testing were prepared by injection-molding. The processing conditions are listed in Table II.

Test Procedures

Tensile testing was conducted by a Tensilon STM-T50BP of Orientec Co. The elongation rate was kept at $10 \, mm \, min^{-1}$. The dimension of bar specimen was $1 \times 2.5 \times 50 \, mm$. The same specimen was used to measure the dynamic viscoelasticity by using Rheovibron of Orientec Co. at 110 Hz over a temperature range from room temperature to 200°C. The morphology of the fractured surface of a bar specimen (broken in liquid nitrogen) was examined in a Hitachi S-510 Scanning Electronic Microscope (SEM). The sample surface was coated with gold by sputtering. Infrared spectrum was used with a JASCO FT-IR 5000 Spectrometer to survey the intermolecular chemical reaction between the components. The sample used in IR was the component of PC which was extracted from the blend by a solvent (chloroform) in which PC was selectively dissolved.

The density of injection molded sample was measured at 25°C by a floatation method using a tetrachloromethane–ethanol mixture. The X-ray diffraction was carried out in a Rigaku CN 2013 Diffractometer to compare the degree of orientation of TLCP in the injection sample. The wide angle X-ray diffraction (WAXD) pattern was obtained by a flat-plate camera.

RESULTS AND DISCUSSION

Mechanical Properties

For comparison with the ternary blends, the mechanical properties of the binary blends of PC with three kinds of TLCP were tested. The mechanical data on the binary blends as found in the literature could not be referred here for discussion, as the raw materials and processing conditions in the reported papers more or less different from ours. Thus we tried the same series experiments on our own samples and processing conditions. The ultimate strengths and the initial moduli *vs.* the weight ratio of TLCP to PC for the binary blends of PC/VA, PC/R3, and PC/R5 are shown in Figures 1-a, 1-b, and 1-c, respectively. According to the criteria mentioned in the later part, the properties of PC/VA binary blend (Figure 1-a) were quite poor, being largely lower than the upper bound of modulus for the two-phase blend. Both the blends of PC/R3 (Figure 1-b) and PC/R5 (Figure 1-c) were excellent, as the data surmounted the upper bound of modulus. It had been said that there was an affinity between the PC and the flexible segment in Rodlan TLCP,[24] and our results agreed with this prediction. The criterion for evaluation the systems to be poor or excellent is based on the relationship between the modulus and the composition of two-phase system: the system in which a simple volume additivity relationship or the upper bound of modulus curve holds is evaluated as good, and another system giving the modulus lower than the linear relationship and close to the lower bound is evaluated poor. The evaluation of excellence is given to the
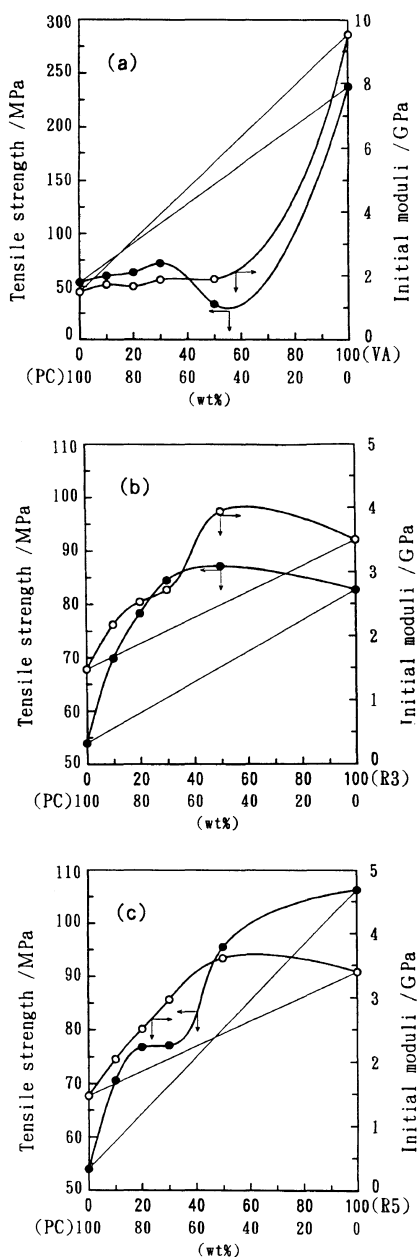
Figure 1. Tensile strength and initial modulus *vs.* TLCP content (wt%) in the binary blends: (a) PC/VA, (b) PC/R3, and (c) PC/R5.

system in which the modulus curve surmounts the upper bound. Quantitative discussion will be given in the special section in the later part.

Figures 2-a and 2-b show the ultimate strengths and moduli *vs.* the weight ratio of the binary blends of two kinds of TLCP, VA/R3, and VA/R5, repectively. The blend of VA/R5 (Figure 2-b) was better to follow the volume additivity of modulus than that of VA/R3 (Figure 2-a), although the moduli in both cases were lower than the upper bound of modulus. It has been known that PHB content of R5 (80%) is larger than that of R3 (60%) and the increased aromaticity in R5 made more compatible with the wholly aromatic VA than R3.

The ternary blend of PC/R/VA showed a dramatically different feature in the modulus to composition relationship. To determine a suitable ratio of the contents, the PC content was kept at the level of 50 wt% or 70 wt%, and the ratio of R to VA was changed. Figures 3-a and 3-b show the results for the PC content of 70 wt% using R3 and R5, respectively. It was found that independent of the PC content, there was a special point of R/VA = 1/9 at which both the strength and modulus reached the maximum values, overwhelmingly surmounting the upper bound. Additionally, if the ratio of R/VA was kept at 1/9, the mechanical properties of PC/R/VA increased with increasing content of TLCP (R + VA) up to 50%. Figures 4-a and 4-b show the results for such blends using R3 and R5, respectively. R5 was more effective than R3.

Dynamic Viscoelasticity

Figure 5 shows the dynamic storage moduli of the binary and ternary blends in which the TLCP content is kept at 50%. For comparison, the storage modulus of PC is also shown in the figure (curve a). At room temperature, the modulus of binary blends of PC/R3 (curve c) was higher than those of PC/VA (curve b) and PC, but it decreased gradually toward the high temperature side and remarkably fell around 70°C. The transition at about 70°C is ascribed to the primary relaxation temperature associated with micro-Brownian motion of PET segment in Rodlan. On the other hand, the
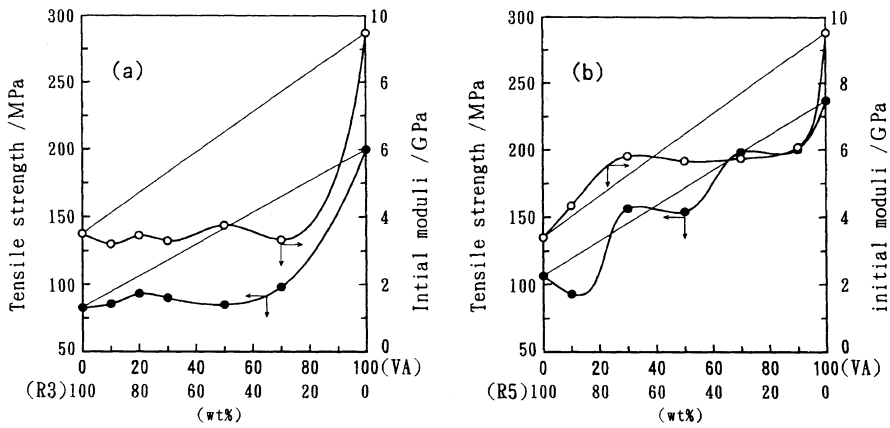
Figure 2. Tensile strength and initial modulus *vs.* content (wt%) in the binary blends of TLCP: (a) R3/VA and (b) R5/VA.
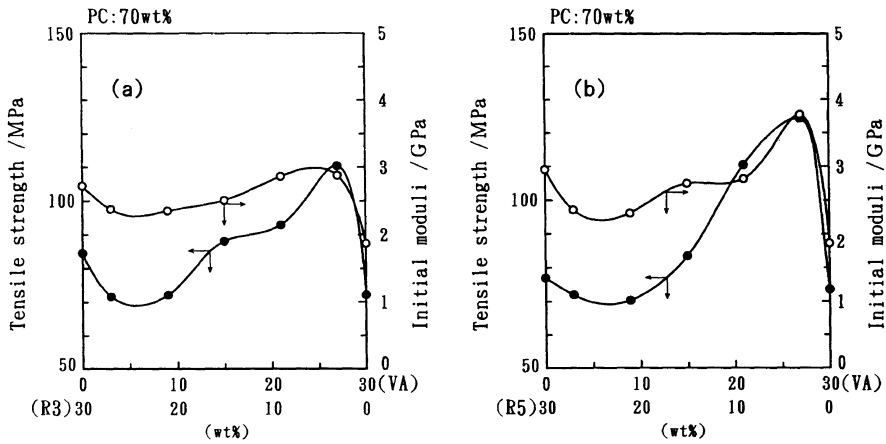
Figure 3. Tensile strength and initial modulus *vs.* content of two kinds of TLCP in the ternary blend for PC content (wt%) = 70 wt%: (a) PC/R3/VA and (b) PC/R5/VA.
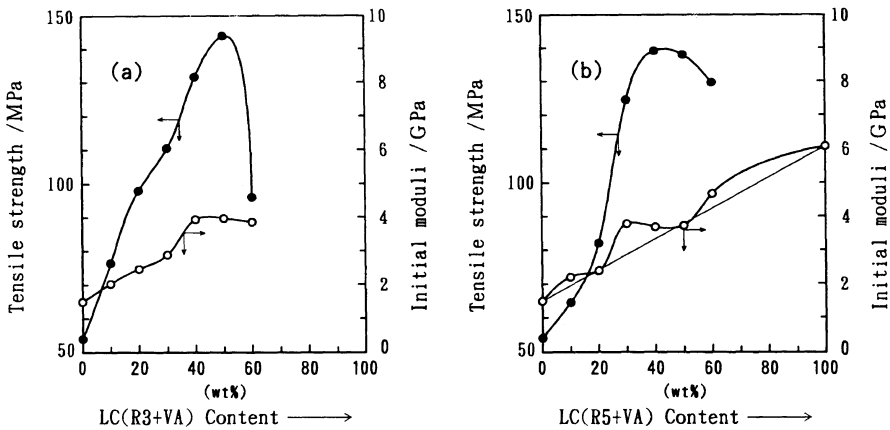
Figure 4. Tensile strength and initial modulus *vs.* TLCP content (wt%) composed of R and VA in the ternary blends for R/VA = 1/9: (a) PC/R3/VA and (b) PC/R5/VA.
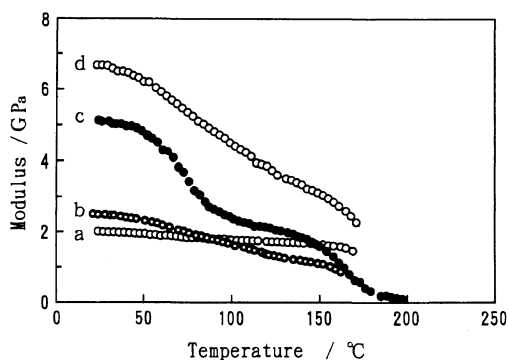
Figure 5. Tensile storage modulus *vs.* temperature: (a) PC, (b) PC/VA = 5/5, (c) PC/R3 = 5/5, and (d)PC/R3/VA = 5/0.5/4.5.
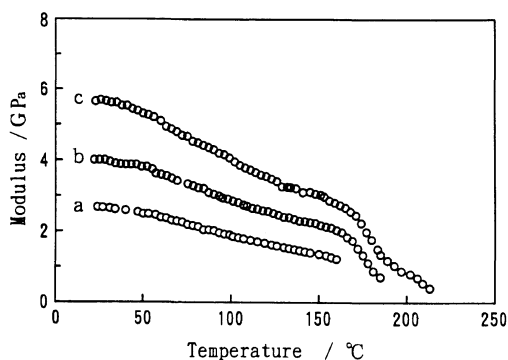

Figure 6. Tensile storage modulus *vs.* temperature for the total TLCP of 30 wt%: (a) PC/VA = 7/3, (b) PC/R3/VA = 7/0.3/2.7, and (c) PC/R5/VA = 7/0.3/2.7.

modulus of the ternary blend PC/R3/VA (curve d) was not only higher than those of the binary blends, but also the change in modulus around 70°C was smaller. The addition of the 3rd TLCP component R3 was concluded to be useful for modulus and thermal endurance. Similar results were found for the samples employing R5.

Figure 6 shows the comparison of the effects of addition of R5 (curve c) and R3 (curve b) on the dynamic moduli at the PC content of 70%. It showed that the 3rd TLCP component of R5 was more effective than that of R3 in improvement of modulus of the binary blend of PC/VA (curve a) over a wide temperature range from room temperature to 200°C. The

results obtained from the ternary blends containing 50% PC were more effective than that of binary blend, but there was no difference between R3 and R5. The increasing content of R5 raised the modulus over a whole temperature range compared with R3; yet in the case of R5 the rate of rise in modulus was not so remarkable as R3. It was also found that for the high content of R5 in the binary blend, the effect of addition of a different 3rd component was not so influential.

Infrared (IR) Measurment

The FT-IR spectra of PC extracted from PC/VA (5/5), PC/R3 (5/5), and PC/R3/VA (5/0.5/4.5) showed only one peak at $1780 \, cm^{-1}$ in the range of 1800—$1700 \, cm^{-1}$, which was characteristic absorption of the carbonate $C=O$ of PC. No peak could be distinguished clearly at $1730 \, cm^{-1}$ and $1740 \, cm^{-1}$, which represented the ester group of TLCP. And also, there was no $780 cm^{-1}$ absorption characteristic of naphthalene group. Thus it could be concluded that there was no significant intermolecular exchange reaction, as far as the processing time was lower than 1 min and the processing temperature was 310°C.

SEM

Figure 7 shows the morphology of the injection-molded sample of the blend PC/VA = 7/3 by SEM. Before injection, the surface showed porous structure and no fibrous structure could be observed. After injection, the surface showed an orientated fibrous texture. But the interfacial adhesion between PC and VA was obviously poor and the both phases were separated. The mechanical properties of the system was also poor (refer to Figure 1), probably due to the poor orientation of the fibril. Figure 8 shows the surface of PC/R3. Although the interfacial adhesion was improved and the fibrils of R3 were clear, the phases were separated. When R3 or R5 was introduced into PC/VA to form a ternary system, the morphologies were changed.
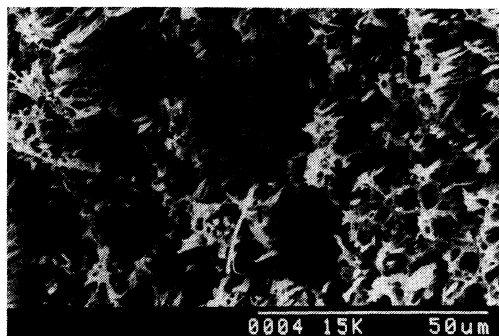
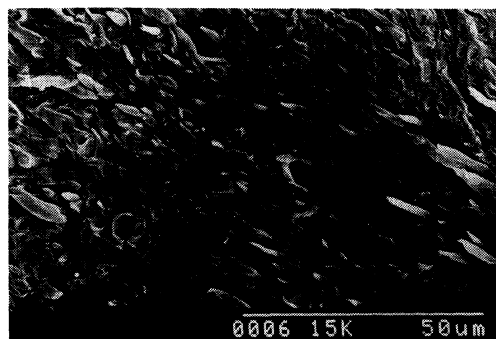**Figure 7.** SEM morphology of fractured surface of injection-molded sample of PC/VA = 7/3.

Figure 8. SEM morphology of skin layer in fractured surface of injection-molded sample of PC/R5 = 9/1.

Figure 9. SEM morphology of skin layer of fractured surface of injection-molded sample for the ternary blends: (a) PC/R5/VA = 7/0.3/2.7 and (b) PC/R5/VA = 5/0.5/4.5.

Figures 9-a and 9-b are for the injection-molded samples of PC/R5/VA = 7/0.3/2.7 and 5/0.5/4.5, respectively. The TLCP fibrils became finer and longer, and like the pure TLCP, the sample bar showed a skin-core structure, still indicating a phase-separation. When the morphologies shown in Figures 9-a and 9-b were compared, the fibrils formed in Figure 9-a were thinner and longer (diameter $\sim 2\,\mu$m) than those formed in Figure 9-b (diameter $\sim 5\,\mu$m). This fact suggested that the orientation of TLCP was more effectively improved in the ternary blend of PC/R5/VA = 7/0.3/2.7 (Figure 9-a) than that of PC/R5/VA = 5/0.5/4.5 (Figure 9-b), perhaps due to the frictional effect at the interface between the melts of TLCP (mainly VA) and PC during injection molding. The frictional force would
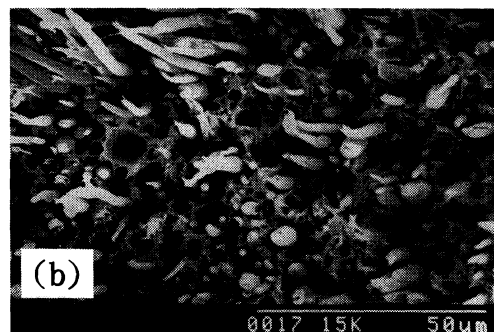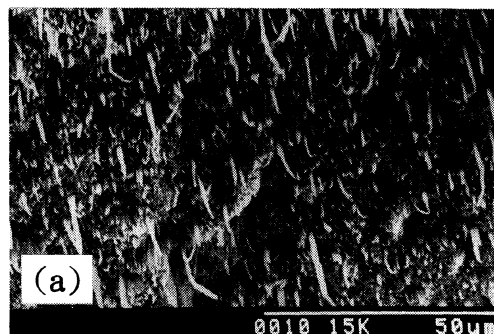
be generated by the intermolecular force between both components. R3 or R5 was known about their partial miscibilities with poly(butyleneterephthalate) in a special solvent.[7] This fact supported the stronger molecular affinities of R3 or R5 to PC than that of VA. Thus, it may be concluded that about 10 wt% of R3 or R5 plays a function of compatibilizer for both the PC and VA components, resulting in the improved orientation of VA in the PC matrix through shear deformation. In this meaning the 3rd TLCP component of Rodrun might be said as an "orientation-providing component for TLCP" in the TLCP-reinforced plastics. The improved orientation of TLCP in PC was supported by the data on the X-ray diffraction, and the two-phase mechanical model for explanation of modulus as mentioned in the following section.
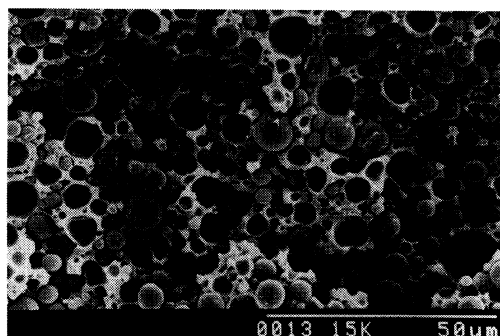
Figure 10. SEM morphology of fractured surface of the blend-extrudate of the ternary blend of PC/R5/VA = 5/0.5/4.5.

Figure 10 shows the SEM photograph of blend-extrudate of PC/R5/VA = 5/0.5/4.5, in which TLCP took spherical shape in the PC matrix. The sphere was composed of many anisotropic domains and statistically isotropic although each domain took a nematic structure. When the pellets cut from a blend-extrudate were injection-molded, the spherical domain was deformed and elongated along the direction of the high shear stress, which was generated by high draw ratio as the diameter of the cylinder was 16.5 mm and the gate diameter of the mold was 1.0 mm.

Explanation of Morphology Based on Crystallization Kinetics of Rod Molecules

The SEM observation revealed that the introduction of the 3rd TLCP component (R3 or R5), which was effective in improvement of mechanical properties of the blend of PC/VA, made the TLCP fibrils (VA) finer in diameter and longer in length. Such an effect of the 3rd TLCP component was suspected to be closely related to the interfacial energies between TLCP and PC. To prove this prediction, it was necessary to deduce the relationship based on the crystallization kinetics.

The thermodynamic properties and crystallization kinetics of TLCP were reported by several authors, among which the most detailed thermal measurements and analysis were made by Kamal et al.[18] The material they used was a single component of TLCP similar to Vectra A and the isothermal crystallization process was analyzed. Their results were difficult to apply to our case since our system was the blend of two or three components, and the morphologies and mechanical properties in this paper were on the specimen prepared by injection-molding. Thus, the discussion on the morphology presented here must be made on the crystallization kinetics of the rodlike molecules from nematic liquid crystal state which was formed after shear deformation of the blend-extruded system. As it was difficult to characterize the molecular environment of TLCP in injection molding, we started our discussion from the coexisting state of system of nematic TLCP domain and molten PC matrix.

The free energy of formation of a rod-shape fibril with radius r and length l, ΔF_p, is given by the following equation:

$$\Delta F_p = -\pi r^2 l \cdot \Delta f + 2\pi r l \cdot \sigma_s + 2\pi r^2 \sigma_e \quad (1)$$

where σ_s and σ_e are the surface energies of side and end surface of the fibril, respectively, and Δf is the free energy of fusion of TLCP crystal per unit volume. After primary and secondary differentiation of ΔF_p with respect to r and l, the curved energy surface is found to have a barrier with a saddle point at r^* and l^*, which are given by

$$r^* = 2\sigma_s/\Delta f$$
$$l^* = 4\sigma_e/\Delta f \quad (2)$$

and

$$\Delta F_p^* = \pi r^{*2} l^* \Delta f = 16\pi\sigma_s^2 \cdot \sigma_e/\Delta f^2$$

Equation 1 is entirely the same in its form as the one derived for the primary nucleus of polyethylene single crystal by Lauritzen–Hoffman.[19] The shape of the primary nucleus is rodlike for $\sigma_e > \sigma_s$.

The final shape of crystal must be discussed on the ratio of the growth rates of the secondary
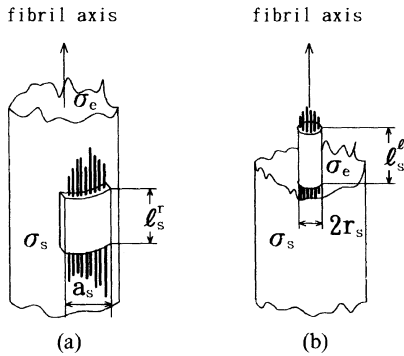
Figure 11. Surface nucleation of rodlike molecules on (a) the side surface and (b) the end surface of a TLCP fibril.

nucleus along the fibril axis, G_l, and the radial direction, G_r. For $G_l \gg G_r$, the TLCP crystal take a rodlike shape. According to Oyama,[20] the problem is solved as follows (refer to Figure 11). The free energy of formation of the surface nucleus on the side surface of TLCP fibril, ΔF_s^r, is given by

$$\Delta F_s^r = -\Delta f(a_s \cdot l_s^r) + 2\sigma_s \cdot l_r^s \cdot b_0 + 2\sigma_e \cdot a_s \cdot b_0 \tag{3}$$

where b_0 is the thickness of monomolecular layer and assumed as unity in the later part. A similar solution for the critical surface nucleus as found in the L–H theory is given by

$$a_s^* = 2\sigma_s/\Delta f$$
$$d_s^{r*} = 2\sigma_e/\Delta f \tag{4}$$
$$\Delta F_s^{r*} = 4\sigma_e \cdot \sigma_s/\Delta f$$

Figure 11-a shows the surface nucleus on the side surface with cricumferential width of a_s and height of l_s. Figure 11-b shows the surface nucleus at the end surface of a fibril with radius of r_s and height of l_s, the free energy of formation of which is given by

$$\Delta F_s^l = -\Delta f(\pi r_s^2 l_s^l) + \sigma_s(2\pi r_s l_s^l) \tag{5}$$

It is noticed that the contribution from σ_e is absent in this case and the critical radius r_s^* is given by

$$\left.\begin{array}{l} r_s^* = \sigma_s/\Delta f \\ \Delta F_s^{l*} = \pi\sigma_s^2 \cdot l_s/\Delta f \end{array}\right\} \tag{6}$$

The ratio of the rates of secondary nucleation along the longitudinal and the radial direction, i_s^l and i_s^r, respectively, is given by

$$i_s^l/i_s^r = \exp(4\sigma_e/\pi\sigma_s l_s) \tag{7}$$

When the relationship of $i = i_0 \exp(-\Delta F_D/KT)\exp(-\Delta F_s/KT)$ is considered, where ΔF_D is the activation free energy for transportation, the diffusion term is assumed to be almost invariant in a nematic molecular environment.

Under the shearing stress, the alignmet of rod molecules in the melt is accelerated and the transportation of rodlike molecule in the transverse direction on the surface is easy, that is, the surface nucleus grows rapidly with the velocity of v for both kinds of nucleus. As G was given by the nucleation rate, i, multiplied by the transportation velocity, v, for the growth of single fibril, it could be concluded that G_l is far larger than G_r to give rise to the fomation of rodlike fibril.

The effect of surface energy σ_s is given by eq 7. With decreasing the value of σ_s, the ratio of nucleation rates along the longitudinal to the radial direction is increased. The shape of fibril with reduced interfacial energy at the side surface becomes finer and longer. The comparison of SEM morphologies shown in Figures 9-a and 9-b with the same magnification indicated the effect of reduction of the side surface energy. The addition of appropriate amount of the 3rd component of TLCP played a role of compatilizer at the interface of TLCP and PC, resulting in reduction of interfacial energy of both components leading to finer fibril.

Density Measurement

Figure 12-a shows the density curve of binary blends of PC/VA and PC/R5, which basically increased linearly with the content of TLCP.
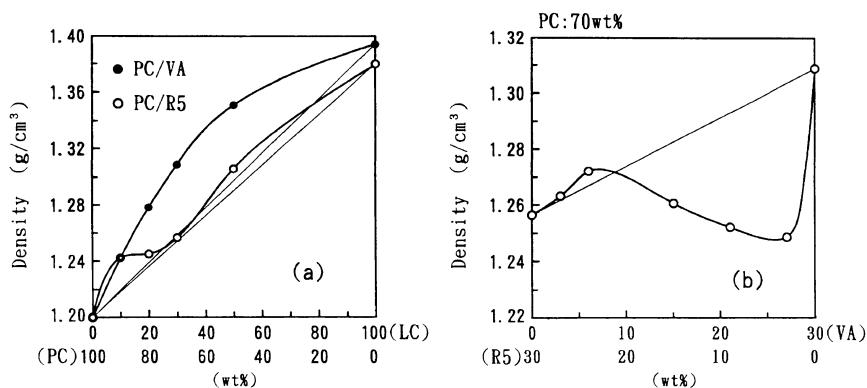
Figure 12. The density vs. composition of the blend at 25°C: (a) binary blend PC/VA and PC/R5 and (b) ternary blend PC/R5/VA when PC content = 70%.

But the density curve of the ternary blend of PC/R5/VA with PC content of 70% was quite different from the binary blend as shown in Figure 12-b. The curve of the density vs. the ratio of R5 to VA deviated toward the lower side from the simple additivity relationship with the change of the composition ratio of R5 to VA. It should be noticed that the density curve changed inversely to the corresponding mechanical properties, that is, when the mechanical property was lower, for example, for PC/R5/VA = 7/0/3, the density was higher; on the other hand, when the mechanical property was higher, for example, for PC/R5/VA = 7/0.3/2.7 and 7/3/0, the density was lower. The reason for the relationship might be explained as follows. The formation of finer fibril resulted in the higher mechanical property due to the improved orientation of TLCP in fibril as proved by X-ray diffraction in the next section. At the high temperatures of injection molding, the longitudinal dimension of the TLCP fibril fit to that of the matrix PC, but when the sample was cooled down close to room temperature in the mold, the residual stress was generated between both components as the thermal expansion coefficient of TLCP was almost zero. The increased residual stress of PC at the interface resulted in generation of many voids which could not be filled up by the floating solution for density measurement. The positive deviation from linear relationship for PC/VA might be related to induced crystallization of TLCP or PC, but the final solution of the problem remained for the future.

X-Ray Diffraction

Figures 13-a, 13-b, and 13-c show the WAXD patterns of the skin part of the sample bars of injection-molded VA, PC/VA = 7/3, and PC/R5/VA = 7/0.3/2.7, respectively. The intensity of the equatorial diffraction of (110) for injection-molded bar of Vectra A was selected to evaluate the orientation of TLCP in the fibril. The width of half maximum intensity was evaluated from an intensity curve scanned along the circumferential direction by use of a photodensitometer. It was known that the very strong diffraction of a strongly annealed Vectra fiber, "Vectran" of Kuraray Co., was indicated in the literature[21] as originated from the (110) crystal plane. The observed spacing of our specimen used for evaluation of orientation was 0.453 nm, which accorded with the value of 0.453 nm for a fiber in the literature. The conventional orientation parameter Q was obtained from the width of half maximum θ according to the following equation:
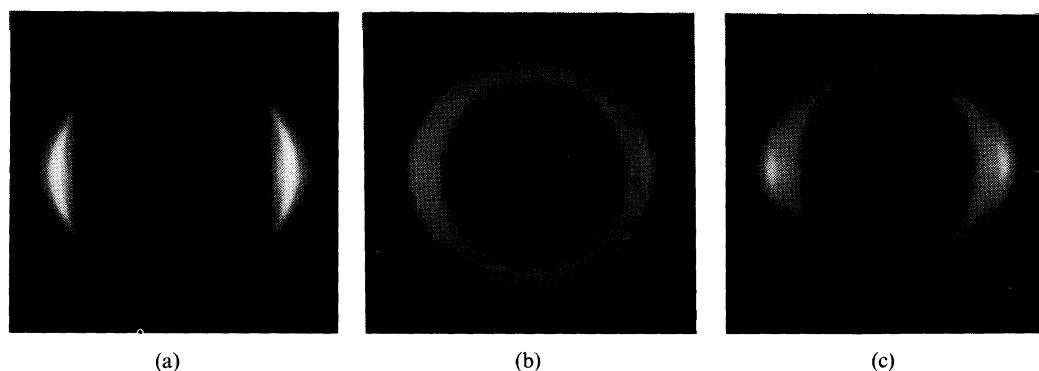
Figure 13. WAXD patterns of the skin part of the bar specimens: (a) VA, (b) PC/VA = 7/3, and (c) PC/R5/VA = 7/0.3/2.7.

Table III. Orientation parameter (Q%)

Sample	VA	R5	PC/VA = 7/3	PC/R5 = 7/3	PC/R5/VA = 7/0.3/2.7	PC/R5/VA = 5/0.5/4.5
Q/%	71.1	74.4	65	81	81	78.9

$$Q = [(180 - \theta)/180] \times 100\% \qquad (8)$$

The results are shown in Table III.

Table III gives the following important conclusions: (1) the orientation of VA in the binary blend of PC/VA is lower than that of pure VA; (2) the addition of R5 to PC/VA gives rise to the improved orientation of VA; (3) the orientation of VA in the ternary blend is higher than that of pure VA; and (4) the orientation of TLCP in PC/R5/VA = 7/0.3/2.7 is higher than that of PC/R5/VA = 5/0.5/4.5. All these conclusions are agreeable when the results of mechanical testing are compared with those in Table III. The effects of orientation of TLCP on the mechanical properties will be explained in the following section in detail.

Explanation of the Relationship between Modulus and Blend Composition

The viscoelasticity of two phase blends had been well evaluated with a mechanical model constructed by connecting two kinds of element over a wide temperature range as far as a morphological change of the blend did not take place.[22] Each element was assumed to have its own modulus and the experimental parameter representing the degree of contribution was empirically evaluated by taking into account of the volume fraction of the component and the morphology. The upper limit of the modulus of the two-phase system was given by the parallel connection of both the elements, through all the composition of the system. On the other hand, the lower limit of the modulus was given by the series connection. The dynamic viscoelasticity of rubber particle-toughened plastics such as ABS resin was quantitatively described by use of volume fraction of rubber and an experimental parameter, representing the extent of contribution in a parallel-series model.

Now the application of two-phase parallel model to the cases of the blends of TLCP and PC was well acceptable when referred to the blend morphology. The modulus of PC and that of TLCP were evaluated separately. When the relationship between the modulus and the

composition for the blend was linear, the case corresponds to the upper limit of modulus represented by a parallel model. The contribution from the TLCP element was evaluated as the highest in this case as far as the modulus of fibril was the same as that of unblended TLCP. But in reality, such cases were rare and the modulus data were higher or lower than the upper bound of modulus.

In the meaning that the contribution from TLCP was low, the blends giving the data lower than the linear relationship was evaluated as "poor" (refer to Figure 1-a). On the other hand, in the reversed meaning as the above, the blends giving the data higher than the linear relationship was evaluated as "excellent" (refer to Figure 1-b). In the ternary system, the behavior for the low content of TLCP showed "good" evaluation according to these criteria (Figure 4).

The blends of TLCP and PC were proved to be of two-phase morphology by FT-IR, SEM observations and X-ray diffraction. One explanation of the relationship between the modulus and the blend composition giving the higher value than the linear relationship was that the orientation of TLCP in the blend was improved by injection molding, resulting in a higher modulus of fibril than that of pure TLCP, and the modulus contribution from TLCP to the whole blend system was larger than that of predicted value from the modulus of unblended TLCP. The relationship was represented by eq 9 and the illustration of geometrical analysis was given by Figure 14:

$$E_c = V_{TLCP}[E^\circ_{TLCP} \cdot f] + V_{PC} \cdot E_{PC} \qquad (9)$$

where E_c is the modulus of the blend, E_{PC} is the modulus of PC, which was assumed not to vary by molding and E°_{TLCP} was an ideal tensile modulus of TLCP along the molecular axis. f is an orientation function, which depends on the condition of injection molding and the composition of the blend in molten state. More strictly speaking, the average value of E_c is to be evaluated by summarizing the contribution

from each layer in the sheet composed of skin and core. Average value of f is given by multiplying the layer thickness by the orientation function of LCP in the corresponding layer. In some cases E_{TLCP} overcame the modulus of unblended TLCP; V_{TLCP} and V_{PC} were the volume fractions of TLCP and PC, respectively.

The term of TLCP employed in eq 9 represented properties of the blend of two kinds of TLCP in the ternary blend. At present the state of coexistence of VA and R3 or R5 could not be clarified by the analytical methods, but the evaluation of the relationship between modulus and composition as seen in Figure 2 indicated a "poor" relationship between both phase of VA and R3 or R5, that was, both kinds of TLCP were immiscible and phase-separated. When the 3rd TLCP component (R3 or R5) was effective in the meaning of giving the excellent mechanical properties, it was forced to conclude that the 3rd TLCP accelerated the orientation of VA as a major fraction of TLCP during injection molding to form a finer and stiffer fibril and raised the modulus of the blend.
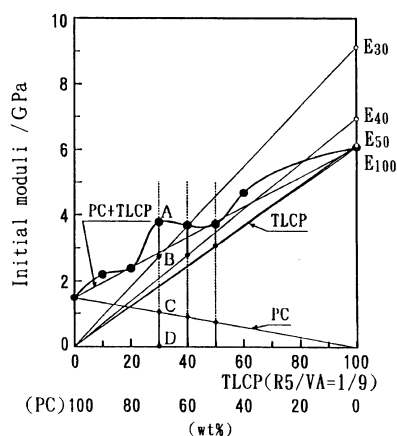

Figure 14. Diagram illustrating the analysis of the modulus-composition curve for the two-phase system of PC and TLCP. E_{30}, E_{40}, and E_{50} are the extrapolated moduli corrected by the contribution from PC modulus for TLCP/PC = 30/70, 40/60, and 50/50, respectively. E_{100} is the experimental modulus for unblended TLCP. Refer to method of analysis described in the text.

Figure 14 shows the method of evaluation of increased modulus of TLCP in the blend based on eq 9. The excellent modulus value of PC/R5/VA = 7.0/0.3/2.7 denoted by point A was corrected to B by substracting the contribution from PC represented by the section of CD from the section of AD. The linear extrapotation of the straight line drawn from the origin to the 100% TLCP gave the modulus of TLCP in fibril of 9GPa, which was larger than the experimentally determined modulus of unblended TLCP 6GPa. The highest modulus of polyarylate fiber was said to be 69GPa of observed value and reported to be 126GPa of observed X-ray modulus.[23] Thus, there would be much more possibilities in increasing the modulus of TLCP in the blend in the presence of the 3rd TLCP component, which is appropriate to be called an "orientation providing component." The evaluation of orientation of TLCP by WAXD shown in Table III well accorded with the order of modulus evaluated by eq 9 or Figure 14.

CONCLUSIONS

Various characterization techniques were employed to clarify the features of the ternary blends composed of PC, Vectra A and a third component of X-7G TLCP. They were blend-extruded followed by injection-molding. The mechanical properties of PC/VA blend were improved dramatically by the addition of a small amount of X-7G TLCP as a third component. The results of FT-IR, SEM, and X-ray diffraction indicated that the blends were always phase-separated no matter whether the third component of X-7G TLCP was used or not, and whether injection molding was conducted or not. No significant intermolecular chemical reaction took place in all cases. The spherical domains of Vectra A became fibrils through injection molding, and the addition of X-7G formed finer and longer TLCP (mainly VA) fibrils. The analysis of the results of WAXD by a conventional method indicated

that the introduction of the third component of X-7G enhanced the degree of the orientation of Vectra A in PC matrix, which led to the great improvement of the mechanical properties of the blends. The modulus of TLCP in the blend was evaluated by a simple geometrical method and found much more increased than that of an unblended injection-molded TLCP by addition of the 3rd component of TLCP.

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