

Additive Effects on Thermotropic Liquid Crystal Polymer Alloys III. Effects of Third Component of Thermotropic Liquid Crystal Polymer on Mechanical Properties of Blends of Ekonol and Polyarylate

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ABSTRACT: The effects of the third component of semi-aromatic thermotropic liquid crystal polymer (TLCP) on the mechanical properties and structure of the blends of polyarylate and a wholly aromatic TLCP were studied. The wholly aromatic TLCP was Ekonol (Sumitomo Chemical Co.) and the semi-aromatic TLCP was Rodlan LC (Unitika Co.). Ekonol (a major component), PAr and Rodlan were blended in the molten state, the extrudate of which was cut and injection-molded. The mechanical properties of the ternary blend were improved by the combination of PAr and Rodlan with Ekonol. SEM revealed that the affinities of the components were improved and finer fibrils of TLCP formed in the ternary blend. X-Ray diffraction analysis showed that the orientation of TLCP fibrils in the blend was enhanced by the addition of the third component of TLCP, which resulted in the improved mechanical properties.

KEY WORDS Polyarylate / Thermotropic Liquid Crystal / Ternary Blends
/ Mechanical Properties / Morphology / X-ray Diffraction Analysis /

It has been well-known that aromatic amorphous polyarylate was a super engineering plastic due to its excellent thermal endurance, impact strength, dimensional stability and transparency. There had been many works on the blends of polyarylate with other engineering plastics like PET, PBT, PC, and so on, mainly to improve their solvent resistance or melt processibility.¹⁻³ Recently, the blends of engineering plastics or super engineering plastics with thermotropic liquid crystal polymers (TLCP) had been studied broadly, which were expected to form "in situ composites."^{4,5} Kiss⁴ studied the blends of Hoechst Celanese Vectra TLCP with a series of engineering plastics and super engineering plastics including polyarylate by using melt blending methods, and found that the mechanical properties of blend of polyarylate with Vectra A (30 wt%) were greatly increas-

ed. And Suenaga *et al.*⁶ reported the blend of polyarylate with a semi-aromatic TLCP of Unitika Co. The frictional properties of the blend of polyarylate with Vectra A were also reported.⁷

On the other hand, it was also interesting to study the blends of TLCP with other polymer composition to reduce the cost and improve thermal, mechanical and processing properties. Suenaga *et al.*⁸ studied the blend of a semi-aromatic TLCP (Unitika LC-5000) with a wholly aromatic TLCP (structurally the same with Ekonol TLCP) and found that the thermal endurance of the blend (HDT) increased with increasing content of the wholly aromatic TLCP.

It was noticed that both polyarylate and Ekonol possessed high heat resistance, the blend of which might be a way to achieve the balance of the physical properties with cost. In

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our previous papers,^{9,10} we reported the studies of the blends of Vectra A-reinforced polycarbonate and poly(butylene terephthalate) and found the mechanical properties of the blends were improved by addition of a small amount of the 3rd component of TLCP. The addition of the 3rd component of TLCP on the mechanical properties were concluded to be profitable to enhance the orientation of TLCP (mainly Vectra A), resulting in the longer and finer TLCP fibrils. In this paper, we studied the mechanical properties of the blend of Ekonol TLCP used as a major component with polyarylate. The introduction of the 3rd component of TLCP was expected to be helpful to improve the mechanical properties of the blend of Ekonol with polyarylate.

EXPERIMENTAL

Materials

Polyarylate (PAr) was supplied by Unitika Co. (U-polymer U-100). A wholly aromatic TLCP was supplied by Sumitomo Chemical Co. (Ekonol E7000, abbreviated by EK). The semi-aromatic TLCP was supplied by Unitika Co. (Rodlan LC5000, abbreviated by R5). Table I lists the characteristics of these polymers.

Preparation of Blends

All the materials were dried under vacuum

at 100°C for at least 24 h before used. The blends were prepared 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 temperatures at rotor and spinning die for extrusion were 280°C and 300–310°C, respectively. The temperatures of the cylinder and the mold for injection were 310°C and 150°C, respectively.

Test Procedures

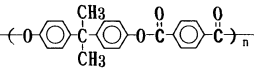
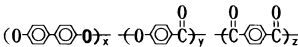
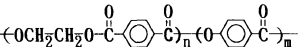
Tensile testing was conducted by a Tensilon STM-T50BP of Orientec Co. The elongation rate was kept at 10 mm min⁻¹. The dimension of bar specimen was ϕ 1.5 × 20 mm. The morphology of the fractured surface of the injection-molded bar was examined by using a Hitachi S-510 Scanning Electron Microscope (SEM). The fractured surface was coated with gold by sputtering. X-Ray diffraction was carried out in a Rigaku CN 2013 Diffractometer to compare the degree of orientation of TLCP in the injection-molded sample. The wide angle X-ray diffraction (WAXD) pattern was obtained by a flat-plate camera.

RESULTS AND DISCUSSION

Mechanical Properties

For comparison, the tensile mechanical

Table I. Characteristics of polymers used in this paper

Materials: (Symbol) (Supplier)	Molecular structure	T_g	T_m
		°C	°C
Polyarylate U-100: (PAr) (Unitika Co.)		193	—
Ekonol E 7000: (EK) (Sumitomo Chem. Co.)		—	310
Rodlan LC-5000: (R5) (Unitika Co.)		70	202

properties of the binary blends were firstly tested. The ultimate strengths and initial moduli vs. the weight ratios of two components for the binary blends of EK/PAr, PAr/R5, and EK/R5 are shown in Figures 1-a, 1-b, and 1-c, respectively. Judging from the criteria presented in our previous paper,⁹ the mechanical properties of EK/PAr (Figure 1-a) and PAr/R5 (Figure 1-b) were allowable, approximately following to the upper bounds of moduli for the two-phase blends. Yet the mechanical properties EK/R5 (Figure 1-c) were poor, being lower than the upper bound of modulus for the two-phase blend. These results revealed that there was a proper affinity between PAr/EK or PAr/R5. On the other hand, the affinity between EK/R5 was poor.

The above results also indicated that the mechanical properties of the EK 7000 were not so good as Vectra, although the thermal endurance of EK was raised. And the mechanical properties of EK were not improved remarkably by blending with PAr or R5. According to our previous papers,^{9,10} the formation and orientation of longer and finer fibrils of TLCP in the blend were very important for the blend containing TLCP to achieve high mechanical properties, and the introduction of the 3rd component of semi-aromatic TLCP to the system of TLCP/thermoplastic was profitable. The stress-strain curves of the ternary blends of EK/R5/PAr with different ratios are shown in Figure 2. For comparison, the stress-strain curves of unblended EK (curve a) and the binary blend of EK/PAr=7/3 (curve b) are also shown in Figure 2. Apparently, the mechanical properties, especially the initial moduli, of EK were enhanced greatly by combination of both PAr and R5. For more clear demonstration, the ultimate strengths and initial moduli vs. composition of the ternary blends are shown in Figure 3. Comparing the binary blend of EK/PAr=7/3 with the ternary blend of EK/R5/PAr=7/1/3, the introduction of a small amount of R5 (9wt%) increased the

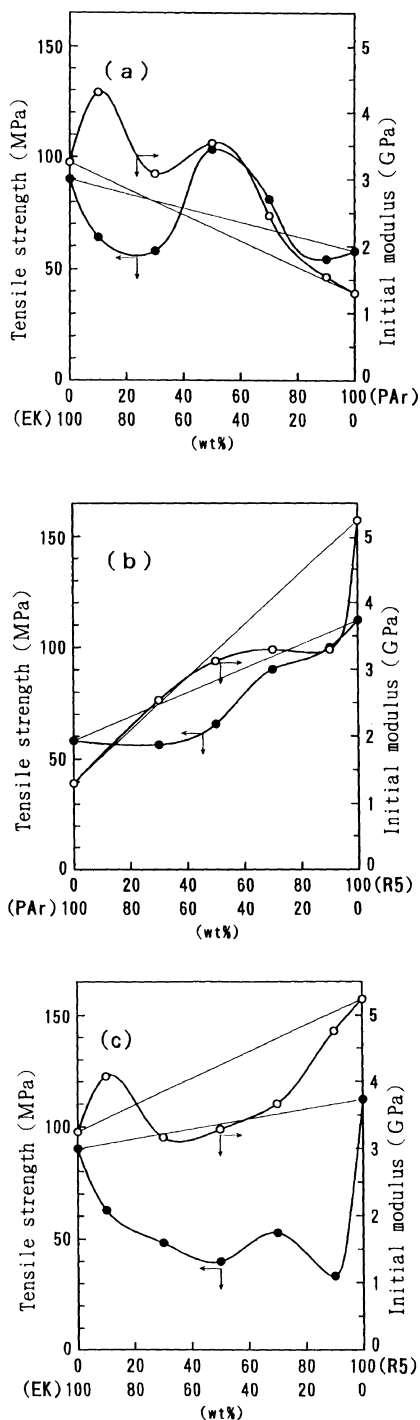


Figure 1. Tensile strength and initial modulus vs. TLCP content (wt%) for the binary blends: (a) EK/PAr, (b) R5/PAr, and (c) EK/R5.

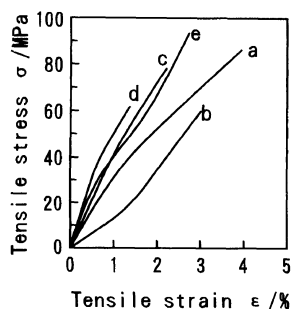


Figure 2. Tensile stress–strain curves for (a) EK, (b) EK/PAr=7/3, (c) EK/R5/PAr=7/1/3, (d) EK/R5/PAr=7/3/3, and (e) EK/R5/PAr=7/5/3.

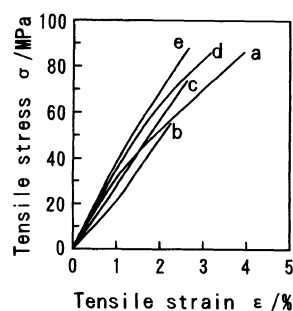


Figure 4. Tensile stress–strain curves for (a) EK, (b) EK/PAr=5/5, (c) EK/R5/PAr=5/1/5, (d) EK/R5/PAr=5/3/5, and (e) EK/R5/PAr=5/5/5.

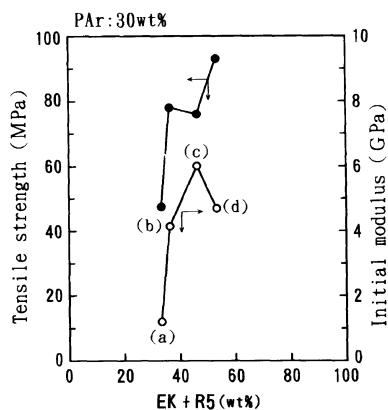


Figure 3. Tensile strength and initial modulus vs. composition for the ternary blends of EK/R5/PAr=(a) 7/0/3, (b) 7/1/3, (c) 7/3/3, and (d) 7/5/3. Blended ratios were recalculated in the figure based on wt% scale.

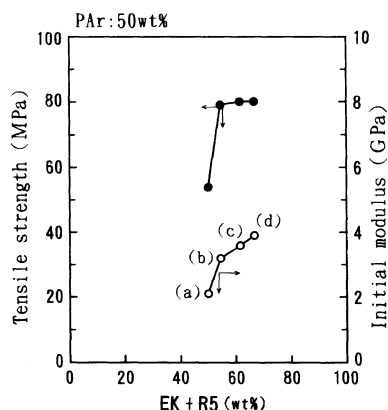


Figure 5. Tensile strength and initial modulus vs. composition for the ternary blends of EK/R5/PAr=(a) 5/0/5, (b) 5/1/5, (c) 5/3/5, and (d) 5/5/5. Blended ratios were recalculated in the figure based on wt% scale.

content of TLCP from 70 wt% to 72.7% and decreased the content of EK from 70 wt% of 63.6 wt%, but increased the initial modulus from 1.35 GPa to 4.17 GPa, which was even higher than that of unblended EK (3.25 GPa). When the content of EK was further decreased, the effect of introduction of 3rd component of R5 to EK/PAr showed the same trends, as the results shown in Figures 4 and 5, although the change of the mechanical properties with the composition became mild. It could be concluded that the 3rd component of TLCP was effective to improve the mechanical properties of EK/PAr. This would be a possible way to achieve the balance of

physical properties with cost.

SEM

The SEM morphologies of the fractured surfaces of injection-molded samples of EK/PAr and PAr/R5 at skin part are shown in Figures 6 and 7, respectively. The two-phase structure could be clearly distinguished for the binary of EK/PAr (refer to Figure 6), indicating that this blending system was phase-separated. Additionally, the interfacial adhesion was poor, corresponding to the poor mechanical properties of this system. Yet, the morphology of the binary blend of PAr/R5 showed a good interfacial adhesion (Figure 7), but the fibrils

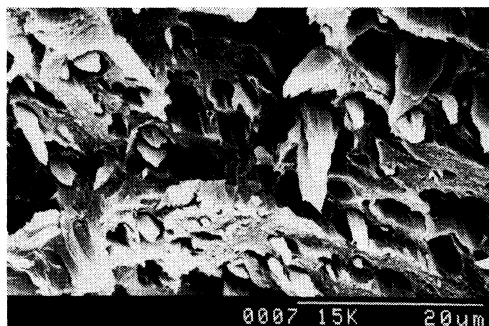


Figure 6. SEM morphology of fractured surface of injection-molded sample of EK/PAr=3/7 at skin part.

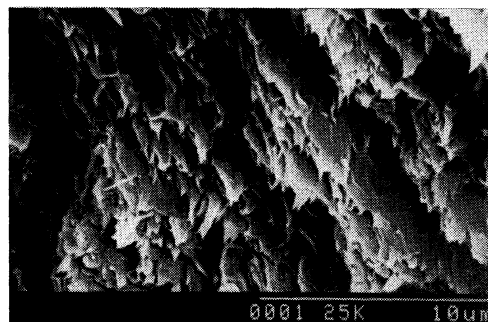


Figure 8. SEM morphology of fractured surface of injection-molded sample of EK/R5/PAr=7/1/3 at skin part.

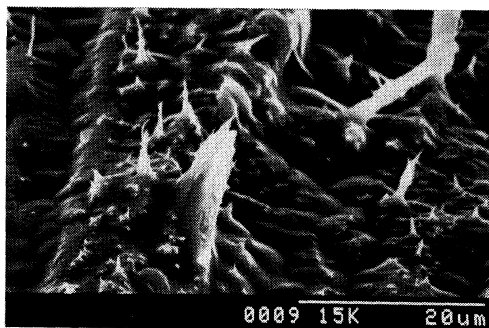


Figure 7. SEM morphology of fractured surface of injection-molded sample of PAr/R5=7/3 at skin part.

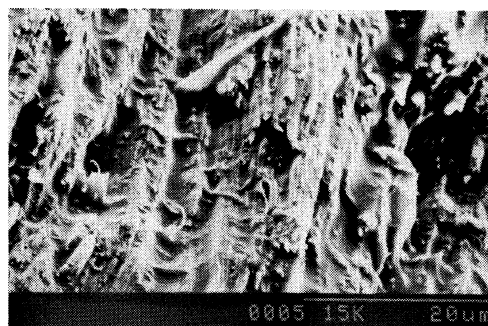


Figure 9. SEM morphology of fractured surface of injection-molded sample of EK/R5/PAr=5/1/5 at skin part.

of R5 in PAr matrix were irregular and not so good for the reinforcement. On the other hand, the ternary blend of Ek/R5/PAr=7/1/3 showed a quite different morphology as shown in Figure 8. Like the pure TLCP, the skin-core structure formed, showing an orientated layered structure in the skin part, in which we could not discriminate separated phase. All these morphologies were profitable to the mechanical properties (refer to Figure 2-c). Figure 9 shows the SEM morphology of the fractured surface of injection-molded sample of the ternary blend of Ek/R5/PAr=5/1/5. The interfacial adhesion was clearly good, in which the layered structure was smeared out. Thus, it could be concluded that the 3rd component of R5 was profitable to improve the interfacial affinity, resulting in the finer TLCP fibrils in the ternary blend.

X-Ray Diffraction

Figures 10-a, 10-b, and 10-c show the WAXD patterns of the injection-molded bars of EK/PAr=7/3, and EK/R5/PAr=7/1/3, respectively. The intensity of the equatorial diffraction of (110) for the injection-molded bar of EK was selected to evaluate the orientation of TLCP in the fibril. The width of half maximum intensity was evaluated from an intensity curve scanning along the circumferential direction by use of a photodensitometer. The conventional orientation parameter Q was obtained from the width of half maximum θ according to the following equation:

$$Q = [(180 - \theta) / 180] \times 100\% \quad (1)$$

The value of Q for EK, EK/PAr=7/3, and

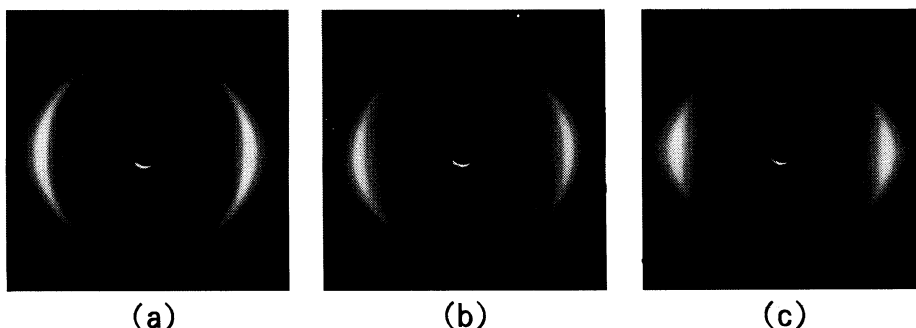


Figure 10. WAXD patterns of injection-molded samples of (a) EK, (b) EK/PAr=7/3, and (c) EK/R5/PAr=7/1/3.

EK/R5/PAr = 7/1/3 were 70.6%, 66.6%, and 77.8%, respectively. Apparently, the order of the orientation parameters corresponded to the order of the mechanical properties, that is, with increasing orientation, the mechanical properties were also increased. Comparing the binary blend of EK/PAr = 7/3 with the ternary blend of EK/R5/PAr = 7/1/3, the degree of orientation of TLCP was enhanced remarkably, which proved the function of R5 as an orientation providing component and explained the improvement of the mechanical properties. This was also agreeable with the results presented in our previous paper^{9,10} for other ternary systems.

CONCLUSIONS

The mechanical properties and the structure of the ternary blend of Ekonol, polyarylate and the 3rd component of TLCP were studied and compared with those of the binary blend of Ekonol and polyarylate. The mechanical properties of the ternary blends were improved significantly by the introduction of the 3rd component of R5. SEM revealed that the affinities between the components in the blends were improved and the finer fibrils of TLCP was formed by introduction of the 3rd component of R5. The analysis of WAXD indicated that the introduction of the 3rd component of R5 was helpful to enhance the degree of orientation of TLCP in the blends,

resulting in the improved mechanical properties. The results of this paper well accorded with those reported in our previous papers in that the 3rd component played the role of orientation providing function. The major difference of this paper from the previous papers was in that the 3rd component of TLCP was used for improving the mechanical properties of TLCP as a major component blended with PAr.

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