Formation and Morphologies of Ethylcyanoethyl Cellulose/Poly(ε-caprolactone) Blending Films

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ABSTRACT: The texture of ethylcyanoethyl cellulose [(ECE)C]/poly(ε-caprolactone) (PCL)/dichloroacetic acid (DCA) solutions and the morphology of the (ECE)C/PCL blending films were studied by polarizing optical microscope. The critical concentration of the (ECE)C/PCL/DCA solutions, at which the mesophase began to appear, was not influenced by the addition of PCL molecules, and the evolution of the cholesteric texture varied with different contents of PCL in the blends. Spherulites with a ringed extinc-

tion pattern in the (ECE)C/PCL blending films were formed below an (ECE)C concentration of 25 wt %. Moreover, the bright band distance of the alternative ringed extinction pattern decreased with increasing (ECE)C concentration. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 550–554, 2004

Key words: liquid-crystalline polymers (LCP); blending; films; morphology; spherulites

INTRODUCTION

Pure poly(ε-caprolactone) (PCL) is a polymer similar to polyethylene in a structural sense. When PCL is blended with other polymers, such as polyvinyl chloride (PVC), polyvinyl butyral (PVB), polycarbonate (PC), and phenoxyl the crystallization temperature (T_c) at which the PCL spherulites demonstrate the ringed extinction patterns becomes much lower, and the ringed extinction patterns become clearer and more regular.[1–6] Keith et al.[7] proposed that the mechanism for the formation of the ring pattern is axial twisting in the lamellae under the influence of surface stress and a cooperative arrangement of twisted lamellae. They also affirmed that thermodynamic compatibility and the existence of specific interactions between the two components are two important factors for the formation of the spherulites with ringed extinction patterns in binary blends.[7]

Until now, the formation of ringed sperulites in the blends of PCL with cellulose derivatives has been scarcel reported. Ma and his colleagues[9] first reported on blends of the PCL and ethyl cellulose (EC) and researched the interaction and compatibility between PCL and EC by Fourier transform infrared and differential scanning calorimetry (DSC). However, studies on the mesophase texture evolution when PCL blends

with the lyotropic liquid crystal have seldom been reported.

Ethylcyanoethyl cellulose [(ECE)C] is a cellulose derivative that has a semirigid chain and can form a cholesteric mesophase in many solvents, such as dichloroacetic acid (DCA), acrylic acid (AA), and styrene.[10,11] Further, it shows multitexture behavior in the solutions. In this study, the cholesteric texture evolution of (ECE)C/PCL/DCA solutions and the morphologies of (ECE)C/PCL blending films were examined simultaneously.

EXPERIMENTAL

The (ECE)C used in this research was prepared by the reaction of EC and acrylonitrile.[10] The molecular formula of the (ECE)C is shown in Figure 1.

The degree of substitution for ethyl was about 2.1, and the degree of substitution for cyanoethyl was about 0.35, which was calculated from the nitrogen content of (ECE)C, measured by elementary analysis (Heraeus, CHN-O-RAPID, Germany). The number-average molecular weight (M_n), of (ECE)C, measured by a gel permeation chromatography (GPC, Waters-209, USA) with tetrahydrofuran as the solvent and polystyrene as the standard material, was 7×10^4. DCA and chloroform were chemically pure reagents. PCL was purchased from the Aldrich Co., and its M_n was 42,500 and its weight-average molecular weight was 65,000.

The (ECE)C/PCL/DCA solutions were prepared in glass vials to investigate the cholesteric texture.
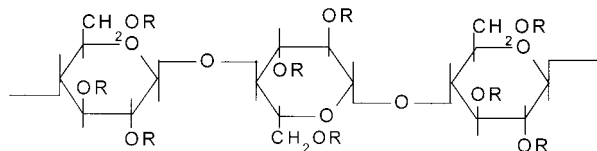
Figure 1 Molecular formula of (ECE)C.

(ECE)C and PCL were mixed with DCA at room temperature, and the solutions were sealed in a test tube. The (ECE)C concentration was kept at 26 wt % with respect to the solvent DCA for the solutions, and the amount of PCL in the solutions was 5, 10, or 15 wt% with respect to the (ECE)C. The solutions were laid aside at room temperature for over 1 week, and then, they were sandwiched between a microscope slide and a cover glass to form a solution film about 20–40 μm thick, and the specimen was sealed with solid wax. The textures of the (ECE)C/PCL/DCA cholesteric liquid-crystal solutions were observed by polarizing optical microscopy (POM; Leitz Orthoplan POL, Germany) after the specimen had been stored at room temperature for 24–48 h.

To prepare the (ECE)C/PCL blending films, we mixed (ECE)C, PCL, and chloroform in a three-necked flask, which was equipped with a mechanical stirrer, a condenser, and a thermometer. The solution was stirred at 323 K for 1 or 2 h to form a homogenous system, and then, the blending films were cast from the solutions. The blending films were dried at room temperature to remove the majority of the solvent, and the residual solvent was removed in vacuum stove for 4 days at 323 K. The morphology of the PCL spherulites in the blends was observed by POM (Orthoplan-Pol, Leitz). The blending film was sandwiched by two clean cover glasses and transferred into another hot stage at a selected T_c to grow the spherulites after it was melted. The morphology of the blending films were observed by POM (Orthoplan-Pol, Leitz). The thermal behavior of the blending films was measured by differential scanning calorimetry (DSC) (Netzsch DSC 204, USA).

RESULTS AND DISCUSSION

Texture evolution of the cholesteric mesophase in the (ECE)C/PCL/DCA solutions

The critical concentration at which the cholesteric mesophase begins to appear can be determined by refractometry[12] because the refractive index increment (n) with the concentration (c; dn/dc) will be changed when the liquid crystalline phase appears in the solution. Figure 2 shows the plots of n versus the total polymer concentration. It was clear that the critical concentration of the total polymers in the (ECE)C/PCL/DCA solution was almost the same as that in the (ECE)C/ DCA solutions. In other words, the PCL addition showed a relatively small effect on the tendency to form a cholesteric phase. According to the Flory's theory on ternary systems consisting of a solvent, a rigid rod solute, and a randomly coiled polymer,[13] the effect of dilution by the soft component may be largely compensated by the hostility of the isotropic phase to rigid sequences. Therefore, we deduced from the results that the critical concentration of the mesophase formation was remarkably dependent on the nature of the polymer and the solvent other than the addition of the randomly coiled polymer PCL in the ternary system of the (ECE)C/PCL/DCA solution.

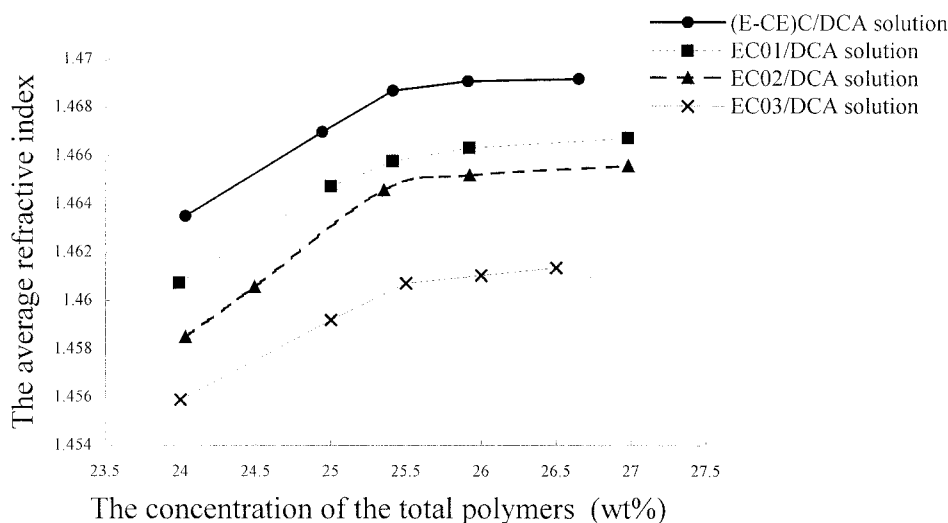Figure 3 shows the texture of the (ECE)C/PCL/ DCA solutions. The mosophase in the (ECE)C/DCA

Figure 2 Plots of n versus the polymer concentration of the (ECE)C/PCL/DCA solutions with different polymer compositions.
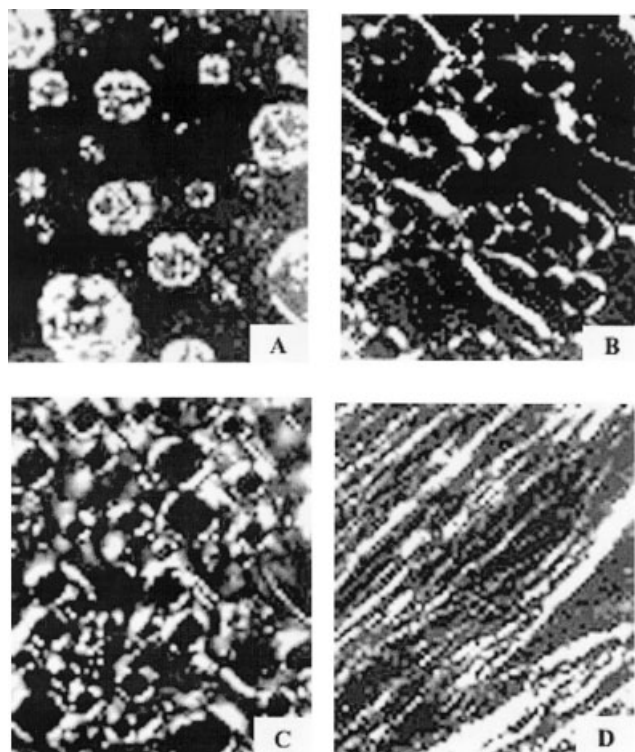
Figure 3 POM micrographs of the (ECE)C/PCL/DCA solutions. The (ECE)C concentration was 26%, and the PCL concentrations were (A) 0, (B) 5, (C) 10, and (D) 15%.

solutions exhibited a disk-like texture at a concentration of 26%. With the addition of PCL, the evolution of the cholesteric texture was probed in the sequence of the shileren, polygonal, and planar textures by increasing the concentration of the PCL from 5 to 15 wt% [respective to (ECE)C, where the (ECE)C content was kept at 26% in the solution. In the (ECE)C/PCL/ DCA solutions, both the (E-CE)C and PCL chains dissolved in the DCA, and the (ECE)C/DCA formed cholesteric domains when the local concentration of the (ECE)C was higher than the critical concentration. The PCL/DCA, however, only formed an isotropic phase, and there was a phase separation between the mesophase and the isotropic phase. With increasing PCL concentration, more (ECE)C chains in the isotropic phase were substituted by the PCL chains, and (ECE)C chains diffused from the isotropic phase into the cholesteric phase, which resulted in an increase of the local concentration of (ECE)C in the anisotropic phase, although the concentration of total polymers in the solution was almost unchanged. Therefore, the cholesteric domains were developed, and the anisotropic aggregates expanded with increasing PCL concentration in the solutions. The addition of PCL in the solution increased the local (ECE)C concentration, and the texture of the cholesteric phase varied from the disk-like texture to the shileren, polygonal, and planar textures gradually with increasing PCL concentration.

Growth of spherulites in the PCL/(E-CE)C blends

When the PCL content was increased beyond 75 wt % in the blending films, the spherulites with alternative ringed extinction patterns appeared in the cast films after an isothermal crystallization. Figure 4 shows the morphology of the PCL spherulites in the blends with different (ECE)C contents. When the (ECE)C content was less than 25% in the blending films, the alternative ringed extinction pattern in the PCL spherulites was observed when the film was crystallized at a temperature of 318 K. However, the frequency of the nucleation of spherulites and the regularity of lamellar organization in the alternative ringed extinction pattern varied with blending composition. Because the (ECE)C component in the blending films was almost amorphous, we believe that in the spherulites with the alternative ringed extinction pattern, the (ECE)C chains concentrated at growth fronts during PCL crystallization and, ultimately dispersed between lamellar crystals in the spherulites with concentrations larger than that in the virgin melt. The adsorption of the (ECE)C chains on both the growth faces and fold surfaces of the PCL crystals may have promoted the PCL chain folding and may have accelerated the crystallization. The influences of the (ECE)C chains on the PCL crystallization may have directly resulted in the regularity of the texture and, changed the direction of the PCL lamellae growth, which may have formed the twist lamellae. The width of the bright band in the alternative ringed extinction pattern decreased linearly with increasing (ECE)C concentration (Fig. 5), and we suggest that the formation and the morphology of the spherulites with alternative ringed extinction patterns were influenced by the amorphous component in the blending films. Similar results have also been found in PCL/PVC,[14] PE/hydroxyethyl cellulose acetate (HECA),[15] and PCL/copoly(styrene-acrylonitrile) (SAN)[16] blends. We propose, therefore, that during the PCL lamellae growth, the increase in the (ECE)C concentration in the front of the crystal resulted in the formation of the (ECE)C concentration gradient from the front of the crystal growth to the blending melt. The growth of the PCL lamellae may have stopped when the (ECE)C concentration was high enough in the local area, but the crystallization of the PCL began again in the area with a lower (ECE)C concentration. Therefore, the formation of the spherulites with alternative ringed extinction patterns in the blending films may have resulted from the twist of the PCL lamellae, the (ECE)C concentration gradient from the front of the crystal growth to the blending melt, or both.

Moreover, the PCL in the blending films formed the spherulites with alternative ringed extinction patterns, in the temperature region from 308 to 318 K when the (ECE)C concentration was less than 25%. This indi-
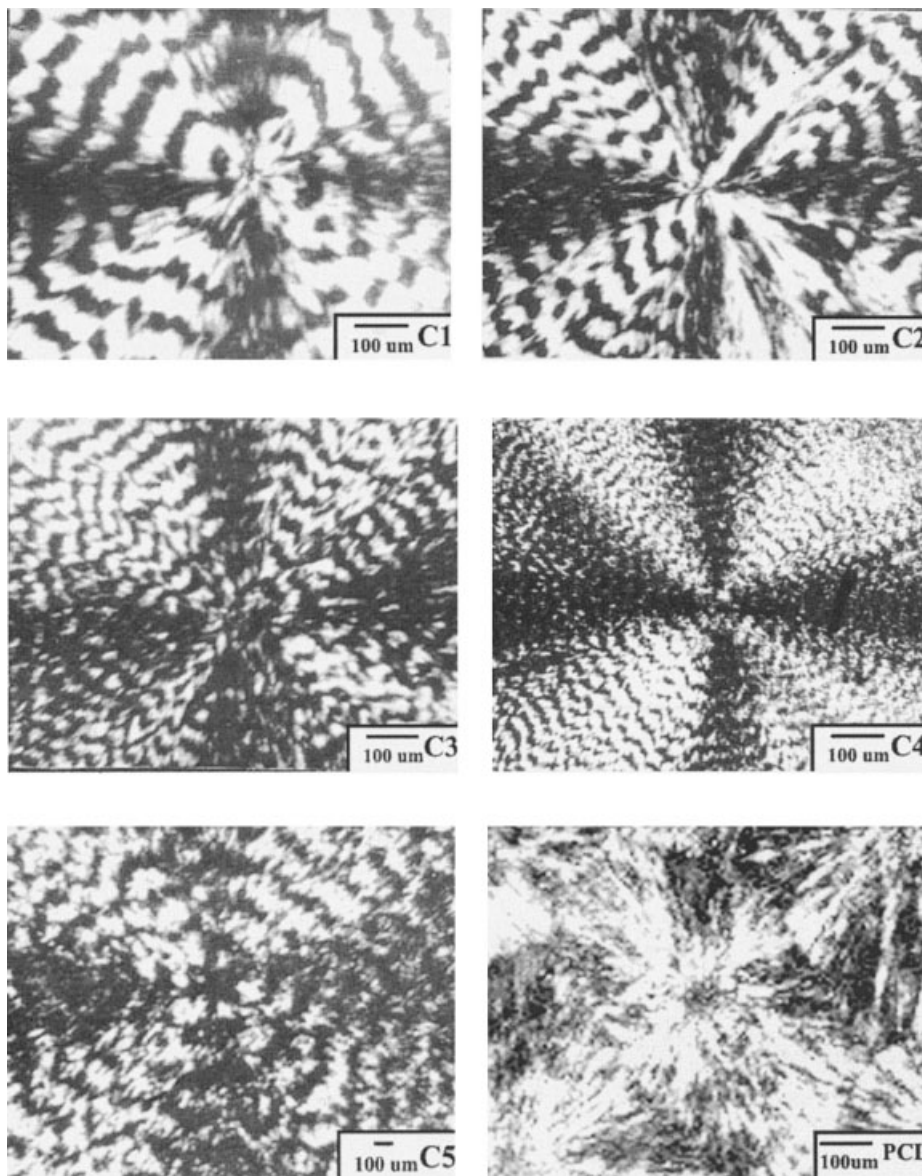
Figure 4 POM micrographs of the (ECE)C/PCL blending films after isothermal crystallization at 318 K. The compositions of the (ECE)C were (C1) 5, (C2), 10 (C3) 15, (C4) 20, (C5) 25, and (PCL) 0%.
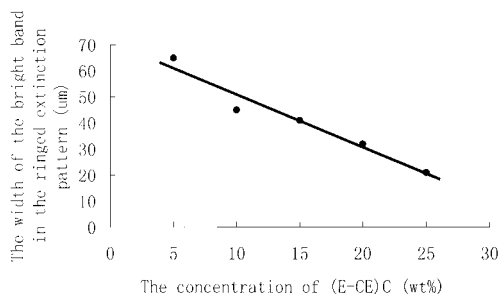

Figure 5 Plot of the width of the bright band in the alternative ringed extinction pattern versus the (ECE)C concentration in the blending films.

cates that the addition of (ECE)C significantly decreased the T_c at which PCL formed spherulites with alternative ringed extinction patterns and improved the formation of the PCL ringed spherulites. It has been reported[1-6] that the amorphous second components in the miscible or partially compatible blends may influence the morphology of the PCL spherulites. We suggest, therefore, that the addition of (ECE)C also improved the formation of the PCL spherulites with alternative ringed extinction patterns.

The DSC results of (ECE)C/PCL blending films with different compositions are listed in Table 1. There was only one glass-transition temperature (T_m) which was the PCL T_g in the blending system, and it increased with the addition of (ECE)C. However, it is

(E-CE)C/PCL	T_g (K)	ΔC_p^* (J/g · K)	T_m (K)	ΔH (J/g PCL)	T_c (K)	ΔH_c (cal/g PCL)
0/100	203	—	332.15	89.83	314.25	68.64
5/95	205.25	0.072	326.84	86.36	309.07	65.21
10/90	205.45	0.060	325.90	81.35	307.83	58.35
15/85	205.95	0.055	324.86	79.45	307.64	53.59
20/80	205.95	0.055	324.08	68.35	305.37	51.71
25/75	206.15	0.050	324.05	65.98	305.14	47.53

almost unchanged with increasing (ECE)C content. The melting temperature (T_m) and T_c of PCL in the (ECE)C/PCL blending films decreased obviously compared to those of the pure PCL. Furthermore, both T_m and T_c of the PCL slightly decreased with increasing (ECE)C content. The enthalpy difference, ΔH, of both melting and crystallization decreased when (ECE)C was added to the PCL and with increasing (ECE)C content. This means that the crystallinity of the PCL in the blends decreased with increasing (ECE)C composition. We suggest, from DSC measurements, that the crystallization of the PCL in the blending films was more difficult than that in the pure PCL and that the addition of (ECE)C obviously reduced the crystallization ability of the PCL. The weakening of the crystallization ability in blending films is a typical feature of miscible or partial miscible polymer systems,[17] and varies with variation in the compatibility of the blends.

CONCLUSION

The morphologies of cholesteric (ECE)C/PCL/DCA solutions and (ECE)C/PCL blending films were observed by POM. The texture of the cholesteric mesophase gradually changed from a disk-like texture to shileren, polygonal, and planar textures gradually with increasing PCL concentration, although the critical concentration, at which the mesophase began to appear, was almost unchanged by the addition of PCL

in the solutions. However, the PCL spherulites with alternative ringed extinction patterns appear in the (ECE)C/PCL blending films at the crystallization region of 308–318 K when the PCL content was greater than 75 wt % in the blends, which indicated that the addition of (ECE)C significantly decreased the T_c at which the PCL formed spherulites with alternative ringed extinction patterns.

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