

Effect of Swelling on the Cholesteric Structure of Ethyl-Cyanoethyl Cellulose/Crosslinked Poly(acrylic acid) Composite Films

Xiaohua Wang,¹ Linge Wang,^{1,2} Yong Huang^{1,2}

¹Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China

²State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 26 December 2002; accepted 26 September 2003

ABSTRACT: The swelling behavior of ethyl-cyanoethyl cellulose [(E-CE)C]/crosslinked poly(acrylic acid) [PAA] cholesteric liquid crystalline composite films and the structural variation of the cholesteric phase during the swelling and the drying process were studied. It was found that the wavelength of the selective reflection of the composite films was shifted to the long wavelength direction during swelling. Both the pitch of the cholesteric phase and the distance between neighboring molecular layers were increased, and the helix axis was inclined after swelling. Moreover, the

swelling behavior of the composite films in water was reversible, which means that the optical properties and structural characters of the films could be changed back to their original states after the films were dried from the equilibrium swelling state. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3574–3578, 2004

Key words: liquid-crystalline polymers; composites; swelling; structure

INTRODUCTION

Cholesteric liquid crystalline polymer (LCP) is one of the most interesting topics in the field of polymers, because many natural biomacromolecules such as polypeptide, cellulose, viruses, RNA, and DNA can form the cholesteric liquid crystalline (LC) phase. Cholesteric LC also shows characteristic optical properties, such as selective reflection, circular dichroism, and strong optical rotatory dispersion for bearing a particular periodic helical structure. For lyotropic cholesteric LCs, the cholesteric structure and optical properties are sensitive to the concentration, solvent, temperature, effects of external fields, and swelling.^{1–6} Moreover, the swelling behavior depends on the composition, solvent, temperature, etc.^{7–12} It has been found by Suto and Inoue⁷ that the optical rotation of cholesteric liquid crystal is changed during swelling in water for crosslinked hydroxypropyl cellulose films filled with cellulose powders. Suto and his coworkers also reported that the temperature and the solvent can strongly affect the swelling behavior of hydroxypropyl cellulose.¹¹ However, details of the variation of

cholesteric structure in the swelling process are still ambiguous.

Ethyl-cyanoethyl cellulose [(E-CE)C], which is a cellulose derivative with two different ester groups, ethyl and cyanoethyl, can form cholesteric liquid crystalline solutions in many organic solvents, such as dichloroacetic acid (DCA) and acrylic acid (AA).¹³ Furthermore, the cholesteric order in the (E-CE)C/AA cholesteric LC solution can be solidified in (E-CE)C/poly(acrylic acid) (PAA) composites by photopolymerizing AA.¹⁴ (E-CE)C/crosslinked PAA composites can be prepared by adding the crosslinking agent into the solutions before polymerization. In this paper, the swelling and drying process of (E-CE)C/crosslinked PAA composites at room temperature were studied and the variation of the structure of the cholesteric phase during the swelling process was discussed.

EXPERIMENTAL

Materials

The (E-CE)C was prepared by the reaction of ethyl cellulose and acrylonitrile.¹⁵ The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.37, respectively, determined by an elemental analysis (CHN-O-RAPID, Heraeus, Germany). The number average molecular weight of (E-CE)C, M_n , measured by a gel permeation chromatograph (GPC) (Waters-ALC-244-GPC) and calibrated by the stan-

Correspondence to: Y. Huang (yhuang@cashq.ac.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number 29925411.

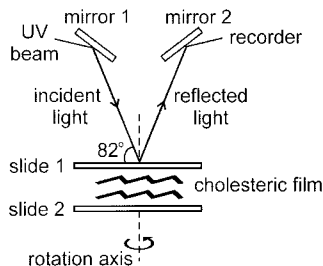


Figure 1 Apparatus set-up of the measurement of the reflection spectra for the composite films. The fixed angle between the incident light and the sample plane was 82° .

dard polystyrene, was 7×10^4 . AA was a chemically pure reagent. Benzoin ethyl ether was a chemically pure reagent and used as the initiator. Divinylbenzene was used as the crosslinking agent and was a chemically pure reagent.

Preparation of (E-CE)C/PAA composite

The (E-CE)C/AA solution was prepared by mixing the (E-CE)C, AA, benzoin ethyl ether (4 wt % with respect to AA), and divinylbenzene (15 wt % with respect to AA) at room temperature. The solution then was stored in the dark at room temperature for about 2 weeks to achieve an equilibrium state. The solution was sandwiched between two glass slides and sealed with solid wax and stored in the dark for 4~5 h to achieve films of equilibrium texture. The thickness of the film was about 0.45 mm controlled by a Teflon space. The sample film then was placed in an ice-water bath and irradiated with a high-intensity mercury arc lamp for about 5 min and formed the (E-CE)C/crosslinked PAA composite. The intensity of the mercury lamp was 250 W. The distance between the sample film and the lamp was 5 cm.

Swelling behavior

The (E-CE)C/PAA composite film was swelled in distilled water at room temperature. During the swelling process, the swelling ratio (R_S) was calculated by the equation:

$$R_S = [(M - M_0)/M_0] \times 100\% \quad (1)$$

where M_0 is the original weight of film and M is the weight during swelling. After reached the equilibrium state of swelling, the film was dried in a desiccator over silica gel, with relative humidity of 45%. The calculation of swelling ratio (R_S) in the drying process was similar with that in the swelling process, where M and M_0 were the weight after drying and before swelling, respectively.

The selective reflection of the composite films during the swelling and drying process was measured by a UV-Vis spectrometer (UV-2550, Shimadzu, Japan). The angle between the incident light and the sample film surface is 82° (Fig. 1). Wide-angle X-ray scattering (WAXS) was measured by an X-ray diffractometer (D/max-1200, Rigaku, Japan). The mean refractive index of the film was measured by an abbe's refractometer (2WA, China).

RESULTS AND DISCUSSION

When the concentration is above 33.8 wt %, the cholesteric phase begins to appear in the (E-CE)C/AA solution. When the concentration is above 42 wt %, the (E-CE)C/AA LC solution is a uniform anisotropic phase, and the mesophase generally shows the planar texture, in which the helix axes align perpendicular to the substance film surface. After polymerization of the AA, the (E-CE)C/crosslinked PAA composite films with (E-CE)C content more than 42 wt % show the planar texture and exhibit vivid colors. The maximum wavelength of the reflection of the cholesteric LC solutions, λ_{\max} , decreases with increasing (E-CE)C concentration (Fig. 2).

In the swelling process (Fig. 3), the λ_{\max} increases with swelling time (red shift), the peak of the reflection becomes wider, and the selectivity became worse. Figure 4 shows the time dependence of the swelling ratio (R_S) and the shift of the λ_{\max} . It can be found that the R_S increases very fast in the beginning of swelling and then slows down and approaches to a plateau when R_S is about 17%. It takes about 26 h when the swelling of the composite film is an equilibrium state. Similarly, the shift of λ_{\max} decreases with swelling time and λ_{\max} is not changed anymore after swelling for 26 h. In contrast, in the drying process, λ_{\max} decreases with drying time and the peak of the reflection becomes narrower and the selectivity of the reflection

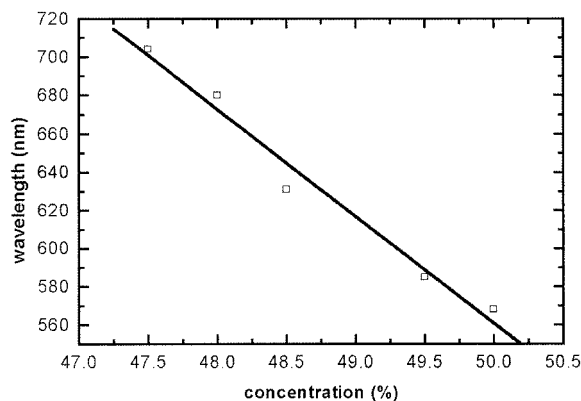


Figure 2 The plot of λ_{\max} of the (E-CE)C/crosslinked PAA composite film versus the (E-CE)C concentration.

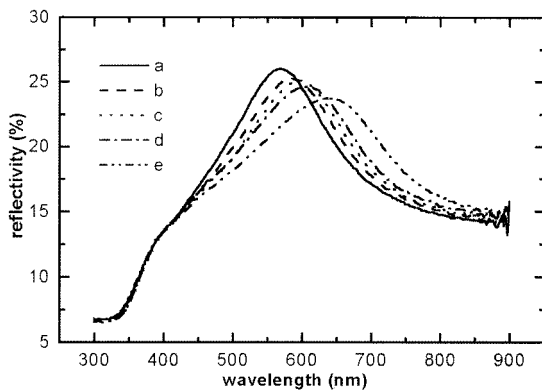


Figure 3 Reflection spectra of 50 wt % (E-CE)C/crosslinked PAA composite film during the swelling process. Swelling times are (a) 0 h, (b) 3.0 h, (c) 5.0 h, (d) 8.0 h, and (e) 26.0 h.

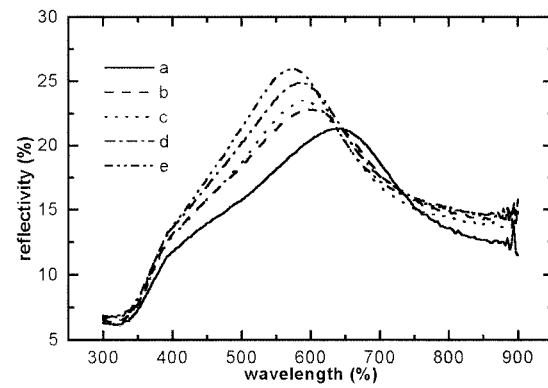


Figure 5 Reflection spectra of 50 wt % (E-CE)C/crosslinked PAA composite film during the drying process. Drying times are (a) 0 h, (b) 1.5 h, (c) 3.5 h, (d) 7.0 h, and (e) 25.0 h.

becomes better (Fig. 5). Figure 6 shows the time dependence of the swelling ratio and the shift of λ_{\max} during the drying process. It can be seen, from Figure 6, that both the R_s and the λ_{\max} of the composite film decrease during the drying process and finally they are not changed anymore after 26 h drying. The weight of the composite film also returns to the original swelling value, after it is dried from the equilibrium swelling state (Table I).

As shown in Table I, the shift of λ_{\max} during the swelling and drying processes is about 80 nm. It is well known that the relationship between the λ_{\max} and the pitch of cholesteric phase (P) can be described by the following equation:¹⁶

$$\lambda_{\max} = nP \sin \varphi \quad (2)$$

where n is the mean refractive index of the system and φ is the angle between the direction of incident light and the molecular layer surface. According to eq. (2),

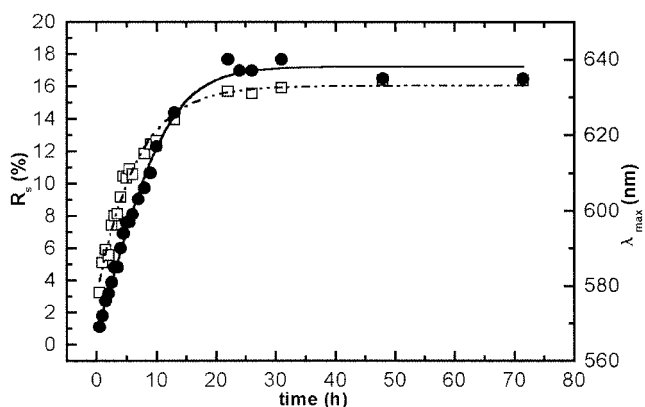


Figure 4 Time dependence of the swelling ratio (\square , dashed line) and the λ_{\max} (\bullet , solid line) during swelling process of 50 wt % (E-CE)C/crosslinked PAA composite film.

λ_{\max} is proportional to n , P , and $\sin \varphi$. Table II lists the value of the mean refractive index (n) of the composite film during the swelling and drying process. The data in Table II indicate that n changes only slightly, which is smaller than 1.1%. It is suggested, therefore, that the variation of n during the swelling and drying processes is not a main factor that results in the λ_{\max} shift.

As shown in Figure 1, when the mesophase shows planar texture, if the helix axis is totally perpendicular to the film surface, the angle φ is always equal to 82° during the rotation of the sample film around the direction normal to the film surface. If the helix axis is inclined, the angle φ will change with the rotation of the sample film, which results in the variation of λ_{\max} . Therefore, the helix axis direction can be determined by measuring the variation of λ_{\max} with the rotation of the film, and the inclination angle can be calculated from the variation of λ_{\max} .¹⁷ By measuring the variation of λ_{\max} during the rotation of the sample film, it is found that the inclination angle is about 4° in the

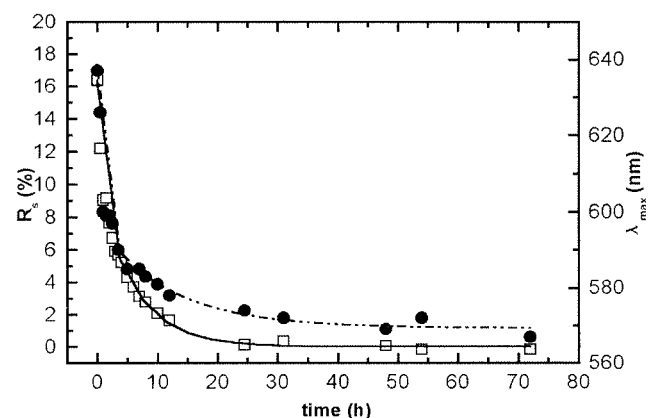


Figure 6 Time dependence of swelling ratio (\square , dashed line) and the λ_{\max} (\bullet , solid line) during drying process of 50 wt % (E-CE)C/crosslinked PAA composite film.

TABLE I
The Variation of Weight, Optical Properties And Structural Characters of 50 wt % (E-CE)C/Crosslinked PAA Cholesteric Composite Film during the Swelling and Drying Processes

	Weight (g)	λ_{\max} (nm)	d (Å)	P^a (nm)	α^b (°)
Original	0.0857	567	8.499	384	0.797
Swelled	0.1005	645	8.581	437	0.707
Dried	0.0861	568	8.499	385	0.795

^a Calculated by eq. (2).

^b Calculated by eq. (3).

equilibrium swelling state. As shown in Figure 4, the variation of the swelling ratio is not proportional to the swelling time. At first, the water molecules are absorbed on the surface of the film and, when the swelling time increases, the water molecules diffuse inside the core of the film, the helix axis is inclined, and the inclination angle reaches the maximum after 26 h of swelling. Similar with the swelling process, the water molecules that were absorbed on the surface of the film are evaporated during the drying process and then the water molecules inside the film are permeated to surface and evaporated. The inclination angle of the helix axis decreases with increases in the drying time and the swollen film can reach to the state before swelling after 26 h of drying. Although the helix axis is inclined during the swelling process, the variation of $\sin\varphi$ causing by the variation of the angle φ is only 1.2%. So the inclination of the helix axis is also not a main factor that results in the shift of λ_{\max} during swelling.

As mentioned above, the influence of both n and φ on the shift of λ_{\max} during swelling and drying is very small. It can be derived from eq. (2) that the main reason for the λ_{\max} shift is the variation of the pitch of the cholesteric phase during the swelling and drying processes. It can be found from Table I that the pitch has changed from 384 to 437 nm after swelling to the equilibrium state and returns to 385 nm after drying from the equilibrium swelling state.

Because the cholesteric LC phase has a periodical layer structure, the distance between neighboring mo-

TABLE II
Mean Refractive Index in the Swelling Drying Processes of 50 wt % (E-CE)C/Crosslinked PAA Composite Film

Swelling time (h)	Mean refractive index	Drying time (h)	Mean refractive index
0	1.4818	0	1.4982
1	1.4819	1	1.4923
2	1.4932	2	1.4941
4	1.4904	4	1.4858
6	1.4953	8	1.4841
24	1.4982	24	1.4825

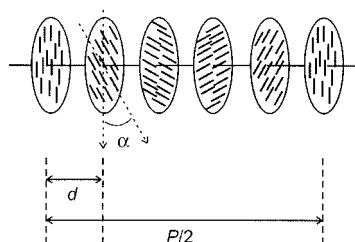


Figure 7 Schematic arrangement of the molecules in the cholesteric structure.

lecular layers, d , can be measured by using the WAXS technique.^{18–22} It has been reported¹⁴ that the cholesteric phase of the (E-CE)C/PAA composite films has a characteristic peak at about $2\theta = 10.0^\circ$ in WAXS spectra. During the swelling and drying process, the peak at about $2\theta = 10.0^\circ$ is preserved, which suggests that the composite film maintains the cholesteric structure. However, as shown in Table I, the distance between neighboring molecular layers (d) increases after the film is swollen to the equilibrium state and returns back to the state before swelling after the water is totally evaporated from the film in the drying process.

The cholesteric phase has a periodical helical structure (Fig. 7) and the relationship of the pitch (P), the distance between neighboring molecular layers (d), and the twisting angle (α) can be described in by following equation:

$$P = d(360/\alpha) \quad (3)$$

Therefore, if any two of the three parameters are obtained, the structure of the cholesteric phase will be clear. The twisting angle between neighboring molecular layers, α , can be calculated by eqs. (2) and (3), and the data of angle α are listed in Table I. It can be seen from Table I that the swelling behavior also results in the variation of the twisting angle (α) of the cholesteric phase and α decreases during the swelling process and increases during the drying process.

The crosslinked PAA network in the composite can absorb water molecules during swelling while the (E-CE)C cannot. The PAA molecules in the composites are dispersed among the (E-CE)C chains and located between and within the ordered (E-CE)C chain layers in the cholesteric structure. The water absorption of the PAA, therefore, may result in the variation of the arrangement and ordering of the (E-CE)C chains in the cholesteric phase. During the swelling process, water molecules infiltrated into the PAA network. The water molecules' permeation into the place between the neighboring (E-CE)C chain layers may result in the increase of d , and the water swelling within the ordered molecular layers and between the neighboring layers may result in the decrease of the hydrogen

bonding interactions between (E-CE)C chains and, therefore, α is decreased. Both the increase of d and the decrease of α result in the increase of the pitch according to eq. (3) and then the λ_{\max} shows a red shift during swelling. During the drying process, oppositely, the pitch decreases with volatilizing the water molecules from the film and the λ_{\max} shows a blue shift because of the decrease of d and the increase of α .

CONCLUSION

The cholesteric order of [(E-CE)C]/crosslinked PAA composite films is significantly influenced by water swelling. During the swelling process, the swelling ratio is increased with the swelling time by the infiltration of water molecules in the film and the wavelength of the selective reflection of the film is increased. The pitch of the cholesteric phase and the distance between neighboring molecular layers increase, while the twisting angle decreases. Moreover, the helix axis becomes inclined during swelling. During the drying process, the swelling ratio decreases with evaporation of water molecules from the film and the reflection wavelength shows a blue shift. Both the pitch and the distance between neighboring molecular layers are decreased, while the twisting angle is increased and the helix axis direction is changed back to align perpendicular to the film surface. The structure

of cholesteric phase can be recovered in the drying process and the swelling behavior of the composite film is reversible.

References

1. Huang, Y. *J Macromol Sci, Phys* 1989, 28, 131.
2. Gunar, V. L.; Derek, G. G. *Polymer* 1985, 26, 1435.
3. Shaikh, V. A. E.; Maldar, N. N.; Lonikar, S. V.; Rajan, C. R.; Ponrathnam, S. *J Appl Polym Sci* 1999, 72, 763.
4. Bak, C. S.; Labes, M. M. *J Chem Phys* 1975, 62, 3066.
5. Patel, D. L.; Gilbert, R. D. *J Appl Polym Sci* 1983, 21, 1079.
6. Wang, L.; Huang, Y. *Macromolecules* 2000, 33, 7062.
7. Suto, S.; Inoue, M. *Polymer* 1999, 40, 2455.
8. Suto, S.; Suzuki, K. *J Appl Polym Sci* 1995, 55, 139.
9. Suto, S.; Suzuki, K. *Polymer* 1997, 38, 391.
10. Zanna, J. J.; Mauzac, M.; Boue, F. *Macromolecules* 1999, 32, 2962.
11. Suto, S.; Kawano, M. *J Appl Polym Sci* 1999, 73, 1015.
12. Zeng, J.; Huang, Y. *Chin J Polym Sci* 1999, 17, 607.
13. Jiang, S. H.; Huang, Y. *J Appl Polym Sci* 1993, 50, 607.
14. Jiang, S. H.; Huang, Y. *J Appl Polym Sci* 1993, 49, 125.
15. Huang, Y.; Chen, M. C.; Li, L. S. *Acta Chim Sinica (Chi)* 1988, 46, 367.
16. de Vries, H. *Acta Crystallogr* 1951, 4, 219.
17. Zhang, G. Q.; Zhou, X. S.; Huang, Y. *Polymer* 2003, 44, 2137.
18. Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss Faraday Soc* 1958, 25, 29.
19. Samuels, R. J. *J Polym Sci, Part A-2* 1969, 7, 1197.
20. Onagi, Y.; White, J.; Feller, J. *J Polym Sci, Polym Phys Ed* 1980, 18, 663.
21. Uematsu, I.; Uematsu, Y. *Adv Polym Sci* 1984, 59, 37.
22. Arici, E.; Greiner, A.; Hou, H.; Reuning, A.; Wendorff, J. H. *Macromol Chem Phys* 2000, 201, 2083.