

## PREPARATION AND PROPERTIES OF ETHYL-CYANOETHYL CELLULOSE/POLYACRYLIC ACID COMPOSITE FILMS WITH REFLECTION COLORS\*

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**Abstract** Ethyl-cyanoethyl cellulose [(E-CE)C]/acrylic acid (AA) becomes a cholesteric liquid crystalline solution with vivid colors when the (E-CE)C concentration is 42 wt%~52 wt%. (E-CE)C/polyacrylic acid (PAA) composites with cholesteric structure were prepared by polymerizing AA in (E-CE)C/AA liquid crystalline solutions. The layers of ordered polymer chains in the cholesteric phase were inclined during polymerization and the degree of the inclination depended on the polymerization temperature and the concentration of the solution before polymerization. The cholesteric structure in the composites could not be changed when temperature was lower than 100 °C. Cross-linking of the PAA in composites improved their water-resistance. The cholesteric order of the composites without cross-linking was destroyed when they were immersed in water. The color derived from the selective reflection of the cholesteric phase of the cross-linked composites turned from blue to red after the composites absorbed water. The color of the composites could be returned to the original one when the absorbed water was removed from the swollen composites.

**Key words** Cholesteric structure, Composites, Selective reflection, Liquid crystalline solutions

### INTRODUCTION

Cellulose and its derivatives are semi-rigid chain polymers and can form lyotropic liquid crystals in appropriate solvents<sup>[1]</sup>, but some of the cellulose derivatives can form both lyotropic liquid crystals and thermotropic liquid crystals. Most of the liquid crystals formed from cellulose and its derivatives are cholesteric and can selectively reflect visible light and exhibit brilliant colors when the cholesteric helical pitch is comparable with the wavelength of visible light<sup>[2]</sup>. The temperature-sensitive effects associated with the selective reflection have been used in a variety of applications, such as thermal indicators and radiation sensors. In some cases, it is desirable that the wavelength of selective reflection be insensitive to temperature. For this purpose, many color films in which the cholesteric structure is frozen have been prepared<sup>[3, 4]</sup>. These films are applicable to passive optical devices, such as circular polarizers, bandpass filters, notch filters and reflective displays.

This kind of films can be prepared in many ways. One of them is to dissolve a liquid crystalline polymer in a vinyl monomer (solvent) to form a lyotropic cholesteric liquid crystalline solution. After polymerization its cholesteric order is frozen, and composite films with cholesteric structure can thus be prepared<sup>[4, 5]</sup>.

We have reported that ethyl cyanoethyl cellulose [(E-CE)C] can be dissolved in acrylic acid (AA) to form a cholesteric liquid crystalline phase which exhibits brilliant colors when the (E-CE)C concentration is within a certain range<sup>[6]</sup>. Furthermore, the (E-CE)C/AA cholesteric liquid crystalline solutions can be easily immobilized

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by photopolymerization<sup>[5]</sup>. In this work, the variation of the cholesteric structure in the system during the polymerization of the solvent AA is studied. The influence of the structure of (E-CE)C polymer chains and the cross-linkage of the polyacrylic acid (PAA) on the properties of the (E-CE)C/PAA composite films are also discussed.

## EXPERIMENTAL

Ethyl-cyanoethyl cellulose [(E-CE)C] was prepared via the reaction of ethyl cellulose, of which the degree of substitution for ethyl was about 2.1, with acrylonitrile<sup>[7]</sup>. The molecular formula of the (E-CE)C is shown in Fig. 1. The molecular weight of (E-CE)C,  $M_n$ , measured by gel permeation chromatography (GPC) (HPLC, Waters, Mode-209) with tetrahydrofuran as the solvent and calibrated by standard polystyrene, was  $21.3 \times 10^4$ . The degree of substitution for cyanoethyl, calculated from the nitrogen content of the (E-CE)C which was measured by elemental analysis (Heraeus CHN Rapid Element Analysis Instrument, Germany), was 0.36. The AA was chemically pure and distilled under vacuum before use.

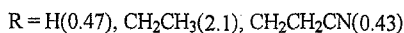
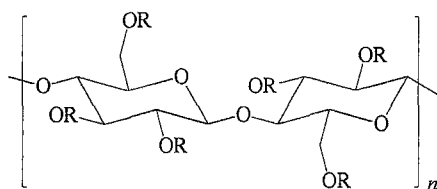


Fig. 1 Molecular formula of ethyl-cyanoethyl cellulose

(E-CE)C/AA liquid crystalline solutions were prepared in glass vials. The desired amount of (E-CE)C, AA and the initiator, benzoin ethyl ether were mixed with a spatula for several minutes in a vial and the mixture was allowed to stand for one week to form a homogeneous solution and was stored in the dark before use. (E-CE)C/AA cholesteric liquid crystalline solutions with 2 wt% benzoin ethyl ether (with respect to AA) were used in photo-polymerization. The solution was sandwiched between two glass slides with a thickness of about 0.3 mm and sealed with wax. The samples were placed in a chamber and irradiated with a 250 W high-intensity mercury arc lamp until complete polymerization occurred to form (E-CE)C/polyacrylic acid (PAA) composite films. Two different polymerization temperatures, 25 °C and 0 °C (ice bath), were used. Cross-linked (E-CE)C/PAA composites were prepared by adding cross-linker, glycol diacrylate (GDA), to the solution before polymerization.

The visible spectra of (E-CE)C/AA liquid crystalline solutions and (E-CE)C/PAA composites were recorded by an UV-VIS spectrophotometer (Specord UV-Vis, Zeiss, Germany). The textures of (E-CE)C/PAA composites at different temperatures were observed by a polarizing microscope (Orthoplan-POL, Leitz, Germany) equipped with a hot stage. The mean refractive index of the solutions and the composites was measured by an Abbe refractometer (2AW, Shanghai Optical Instrument Factory, Shanghai, China).  $T_g$ s of the composites were determined by a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2C). X-ray diffraction study of the composites was carried out on an X-ray diffractometer (D/max-1200, Rigaku, Japan).

## RESULTS AND DISCUSSION

(E-CE)C was dissolved in AA to form the cholesteric liquid crystalline solutions at a concentration above 33.8 wt%<sup>[6]</sup>. Within the concentration of 42 wt%–52 wt%, (E-CE)C/AA liquid crystalline phase in the solutions exhibits a planar texture with brilliant colors derived from the selective reflection of visible light of certain wavelength. The wavelength of the maximum reflection of the solutions decreases with increasing concentration. Figure 2 gives the reflection spectra of the 45 wt% (E-CE)C/AA liquid crystalline solution and the respective (E-CE)C/PAA composite. The peaks in the spectra reveal that the selective reflection due to the cholesteric order

occurs in the visible range and shifts to a shorter wavelength after polymerization with the AA. When the composite was observed by a polarizing microscope, it was found that the composite showed the strongest birefringence at a certain angle. In other words, there is a local orientation for (E-CE)C polymer chains in the composite.

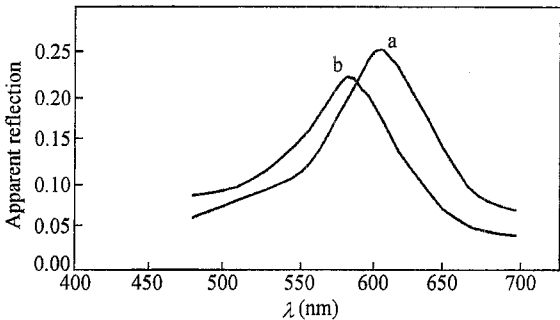


**Fig. 2** Reflection spectra of the 45 wt% (E-CE)C/AA cholesteric liquid crystalline solution and the (E-CE)C/PAA composite prepared from the solution

The selective reflection from the cholesteric liquid crystals can be attributed to the Bragg-like diffraction of visible light caused by the periodic layers of ordered molecules. The wavelength of the strongest reflection can be expressed by the formula<sup>[8]</sup>:

$$\lambda_{\max} = P \cdot n \cdot \sin\varphi$$

where  $\lambda_{\max}$  is the wavelength of the strongest reflection,  $P$  is the pitch of the cholesteric mesophase,  $n$  is the mean refractive index and  $\varphi$  is the angle between the direction of the incident light and the layers of ordered polymer chains. Before polymerization, the liquid crystalline solution shows a planar texture when its concentration is higher than 42 wt% and the layers of ordered polymer chains are parallel to the solution film surface. Thus, the incident light is perpendicular to the layers of ordered polymer chains when it is normal to the solution film surface. Therefore,  $\varphi = 90^\circ$  before polymerization and according to the formula above, at this time,  $\lambda = P \cdot n$ . From the pitch of the cholesteric liquid crystalline phase in the (E-CE)C/AA solutions and the periodicity of the lamellar structure in the (E-CE)C/PAA composites with cholesteric order observed by TEM (Table 1)<sup>[5]</sup>, it is known that the pitch of the cholesteric structure is almost unchanged during the polymerization of the AA in the solution. The mean refractive index of the composites is about 13% larger than that of the corresponding solutions and the ratio of the mean refractive index of the solution and of the composite  $n_s/n_p$  is 0.885~0.89 (Table 2). According to the formula  $\lambda_{\max} = P \cdot n \cdot \sin\varphi$ , the variation of the mean refractive index should result in a shift of  $\lambda_{\max}$  to the longer wavelength direction but actually  $\lambda_{\max}$  shifts towards the shorter wavelength direction. Consequently, the variation of the wavelength of the reflection indicates that the  $\varphi$  is varied and becomes smaller than  $90^\circ$  after the polymerization. The existence of the orientation for (E-CE)C polymer chains in composites, observed by the polarizing microscope, suggests that the layers of ordered polymer chains are not completely parallel to the solution film surface and the layers of ordered polymer chains are inclined.

**Table 1.** Half pitch of (E-CE)C/AA cholesteric liquid crystalline solutions ( $P/2$ ) and periodicity of the lamellation for corresponding composites

| (E-CE)C content (wt%) | 44  | 50  |
|-----------------------|-----|-----|
| $P/2$ (nm)            | 232 | 157 |
| P.S.* (nm)            | 240 | 150 |

\* P.S. is the abbreviation word for the periodicity of the lamellation in composites.

The results of X-ray diffraction confirm the inclination of the layers of ordered polymer chains in the cholesteric phase. Figure 3 shows the X-ray diffraction patterns of the 50 wt% (E-CE)C/PAA composite. The

diffraction peak at about  $2\theta = 9^\circ$  is attributed to the lamellar structure of the cholesteric phase<sup>[9]</sup>. Figure 3(a) is the X-diffraction pattern of the composite when the X-ray is perpendicular to the composite film surface during measurement. There is a very strong diffraction peak at  $2\theta = 9^\circ$ . Figure 3(b) is the X-diffraction pattern of the composite when the X-ray is parallel to the composite film surface during measurement. There is a weak diffraction peak at  $2\theta = 9^\circ$ . If the layers of ordered polymer chains in cholesteric phase are totally parallel to the composite film surface, the diffraction peak at about  $2\theta = 9^\circ$  should not exist in the pattern because there is no periodical lamellar structure in the direction normal to the molecular layers in the cholesteric phase. Figure 3(b), however, indicates that the periodical lamellar structure exists in the direction perpendicular to the composite film surface, suggesting that the layers of ordered polymer chains in the cholesteric phase are not totally parallel to the composite plate surface.

**Table 2.** Refractive indices of (E-CE)C/AA solutions ( $n_s$ ) and (E-CE)C/PAA composites ( $n_p$ ) at  $31.5^\circ\text{C}$

| (E-CE)C content (wt%) | 38.0  | 50.0  |
|-----------------------|-------|-------|
| $n_s$                 | 1.445 | 1.450 |
| $n_p$                 | 1.640 | 1.637 |
| $n_s/n_p$             | 0.887 | 0.886 |

Since the incident light is perpendicular to the composite film surface, the angle  $\varphi$  is smaller than  $90^\circ$ . The wavelength of the reflection shifts towards shorter wavelengths with decreasing angle  $\varphi$ , according to the above formula. The inclination of the layers of ordered polymer chains in cholesteric phase during the polymerization is schematically depicted in Fig. 4. Angle  $\varphi$  can be calculated from the value of  $n_s/n_p$  and  $\lambda_{\max}$  of the solution of the corresponding composite when the incident light is normal to the solution film surface and the composite plane surface. The inclination angle of the layers of ordered polymer chains is  $90^\circ - \varphi$ . The various composites which are prepared at different temperatures and have different (E-CE)C contents are listed in Table 3. The inclination angle is  $36\text{--}46^\circ$  and this result coincides with the results in small angle light scattering (SALS) experiments in which the SALS  $H_v$  pattern changes from X type four-leaf to + type one after the polymerization<sup>[5]</sup>.

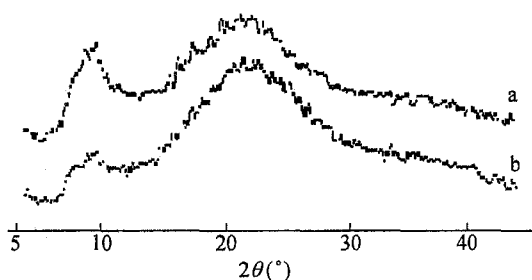


**Fig. 3** X-ray diffraction patterns of the 50 wt% (E-CE)C/PAA composite with cholesteric order. The X-ray beam is (a) perpendicular and (b) parallel to the composite plate surface.

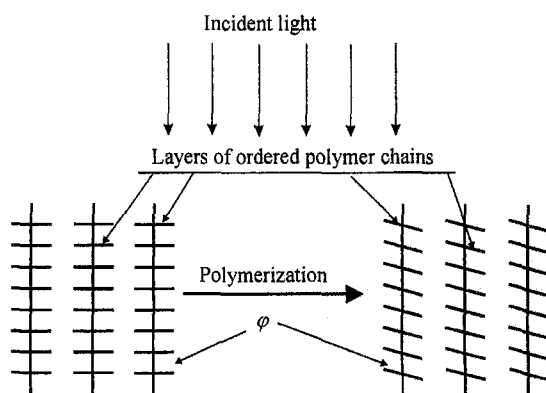


**Fig. 4** Schematic diagram of inclination of successive layers of polymer chains during polymerization, arrows represent the projection of the directions of polymer chains

The data in Table 3 indicate that the inclination of the layers of ordered polymer chains during the polymerization is influenced by (E-CE)C content and the polymerization temperature. Two polymerization temperatures, i.e.  $0^\circ\text{C}$  and room temperature are employed during the polymerization. The inclination angle of molecular layers in the cholesteric phase when the polymerization of the AA is initiated at  $0^\circ\text{C}$  is smaller than that when the polymerization is initiated at room temperature. The inclination angle is also decreased with increasing concentration of the solution before polymerization. As we know, the viscosity of the solution increases with

increasing concentration and decreasing temperature, therefore the inclination of the layers of ordered polymer chains in the cholesteric phase depends on the viscosity of the solution before polymerization. In order to decrease the inclination of the layers of ordered polymer chains and to reserve the reflection colors of the system after polymerization, the solution concentration should be high and the polymerization temperature should be low.

**Table 3.** The inclination angles of the layers of the ordered polymer chains in the cholesteric phase during photo-polymerization

| Polymerization temperature | 0℃   |      | 25℃  |      |      |
|----------------------------|------|------|------|------|------|
| <i>c</i> (wt%)             | 45   | 47   | 42   | 45   | 47   |
| 90- $\varphi$ (°)          | 35.9 | 34.1 | 45.6 | 44.9 | 43.4 |

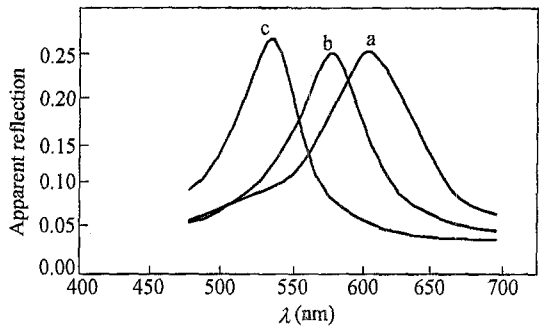


**Fig. 5** Reflection spectra of the 45 wt% (E-CE)C/AA solutions with different GDA, the GDA content (*V/V*%) is (a) 0, (b) 10 and (c) 20

By observing the composites at different temperatures under a polarizing optical microscope with a hot-stage, it was found that the selective reflection of the visible light of the composite films was unchanged until the temperature increases to about 100℃. In other words, the morphology and structure of the composite films is stable at a temperature lower than 100℃. Above 100℃, the intensity of the reflection of the composite films gradually weakens with increasing temperature until 210℃, at which the composite films begin to flow and the reflection colors disappear completely. When the composite films are cooled to room temperature again, the reflection color can not be recovered. This implies that when the temperature is higher than 100℃ the cholesteric structure is gradually destroyed with increasing temperature. The glass transition temperature of the composite films obtained from DSC measurement is about 105~125℃, which is close to the temperature at which the reflection color of the composite films begins to weaken with further increasing temperature. It is suggested, therefore, that the movement of polymer chains in the composite films is restricted and the cholesteric structure remains stable when the temperature is lower than *T<sub>g</sub>* of the composites. When the temperature is over *T<sub>g</sub>*, the cholesteric structure can be destroyed gradually with increasing temperature because of increased mobility of polymer chains in the composite films. The destruction of the cholesteric structure in the films is not reversible when the composite is cooled to room temperature again because (E-CE)C can not be dissolved in PAA to form lyotropic liquid crystals.

PAA can be easily dissolved in water. In order to improve the water-resistance of the (E-CE)C/PAA composite films, glycol acrylate (GDA) was added to (E-CE)C/AA solution before polymerization and, consequently, cross-linked composite films were obtained after photo-polymerization. Figure 5 shows the reflection spectra of 45 wt% (E-CE)C/AA solutions with different contents of GDA. When the GDA content is less than 20 wt% (with respect to AA), the addition of cross-linker does not change the intensity and the selectivity of the reflection of the liquid crystalline solutions. However, this may result in a shift of the reflection wavelength toward a shorter wavelength. Similar to the system without cross-linker, the intensity of the reflection for the system with GDA decreases slightly and the reflection wavelength shifts to shorter wavelengths after

polymerization.

The swelling ratio of 45 wt% (E-CE/PAA) composite films is listed in Table 4. The uncross-linked composite film swells significantly in water and its surface becomes viscous and rough. The swelling ratio of the cross-linked composite film is lower than that without cross-linking and its surface remains smooth after it is immersed in water. The selective reflection of the composite films both with and without GDA shifts toward a longer wavelength after absorbing water. The reflection color gradually turns from blue to red and finally to colorless with increasing swelling ratio. But the intensity of the reflection color of the composite film without GDA becomes weak while that of the cross-linked composite film is unchanged. The reflection color of the cross-linked composite film can return from colorless to red and finally to the original one after the water is gradually removed from the swollen composite film. This is not possible with uncross-linked composite films. This indicates that the cholesteric structure in the uncross-linked composite will be destroyed during immersion, but the cross-linker can inhibit the destruction of the cholesteric order in composite films.

**Table 4.** The swelling rates of 45 wt% (E-CE)C/PAA composite films which have been immersed in water for 30 days

| GDA (V/V%)           | 0  | 10 | 20 |
|----------------------|----|----|----|
| Swelling ratio (%) * | 50 | 30 | 20 |

\* Swelling ratio (%) =  $[(W - W_0)/W_0] \times 100$ ,  $W$  is the weight of the composite film after immersion and  $W_0$  is the weight of the film before immersion.

## CONCLUSIONS

The (E-CE)C/PAA composites with cholesteric order can be prepared from cholesteric liquid crystalline solutions by polymerization of the solvent. The maximum reflection wavelength of the composite films is shorter than that of the solutions before polymerization. The layers of ordered polymer chains in the cholesteric phase are inclined during the polymerization and the degree of inclination is controlled by the polymerization temperature and the concentration of the solution. The inclination angle is small, if the solution concentration is high and polymerization temperature is low, the reflection color of the composite films may be the same as that of the solution before polymerization. The composite films have high thermal stability and the cholesteric structure in the composite films can not be changed when the temperature is lower than 100°C. Cross-linking of AA with GDA in the composite films can improve their water-resistance. The reflection color of the composite films turns from blue to red after they are swollen in water and it can be changed back to the original one after the water is removed.

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