Ethyl-cyanoethyl Cellulose/Poly(Acrylic Acid) Composite: Cholesteric Structure and Optical Property*

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Abstract: Ethyl-cyanoethyl cellulose [(E-CE)C]/poly(acrylic acid) (PAA) composite films were prepared by photopolymerizing acrylic acid (AA) in (E-CE)C/AA cholesteric liquid crystalline solutions. Investigation of the structure and optical property of the (E-CE) C/PAA cholesteric composite and was undertaken by using UV-VIS spectroscopy and TEM. It was found that the wavelength of reflection light was a function of the concentration, the reflectivity was increased with increasing the film's thickness and was decreased quickly when temperature above 160 ℃.

Key words: ethyl-cyanoethyl cellulose; liquid-crystalline polymers (LCP); photopolymerization; composites
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1 Introduction

Cholesteric liquid crystalline polymers (LCPs) is one interesting topics in the field of both polymer science and liquid crystals. Not only many natural biomacromolecules can form cholesteric liquid crystalline phases such as cellulose, polypeptide and DNA, but also the cholesteric LC phase shows characteristic and remarkable optical properties such as strong rotatory power and selective reflection light[1], which have potential for optical application.

The optical property of the selective reflection of cholesteric LC phase is potentially commercial useful. It could served as a polarized light source[2,3], or "photo-copy-safe" materials[4]. In order to apply cholesteric LC phases to these applications, lyotropic cholesteric LC solution was usually formed a solid film to retain the cholesteric structure. The solidified LC film can got by several methods, such as casting[5,6], cross-linking[7-9], quenching[10] and polymerizing solvent of LC polymer solutions[11-15].

Form liquid crystals in the appropriate solvents[16], most of the liquid crystals are cholesteric phase. Ethyl-cyanoethyl cellulose [(E-CE)C], which is a cellulose derivative with two different ether groups, ethyl and cyanoethyl, can forms cholesteric liquid crystalline solution in many organic solvents, such as dichloroacetic acid (DCA)[17] and acrylic acid (AA)[18]. In our previously studies, it has been found that the cholesteric structure of the (E-CE)C/AA solution can be frozen in (E-CE) C/poly (acrylic acid) (PAA) composite by photopolymerization of the solvent AA[12]. As a potential material for application, however, the details of the structure and optical property of (E-CE) C/PAA cholesteric LC composites is not very clear.

In this paper, based on the previously studies, advanced research on the structure selective reflection of (E-CE)C/PAA cholesteric composites was undertook and investigated in detail by using UV-VIS spectroscopy and TEM.

2 Experiment

2.1 Materials

The (E-CE)C was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile[19]. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.33, measured by an elemental analysis (CHN-O-RAPID, Heraeus, Germany). The molecular weight of (E-CE)C, M_w, measured by a gel permeation chromatograph (GPC) (ALC-244-GPC, Waters) and calibrated by the standard polystyrene, was 19×10^4. AA was chemically pure reagent and was distilled in vacuum at 50 ℃ before used.

2.2 Preparation of (E-CE)C/AA solutions and (E-CE)C/PAA composites

The (E-CE)C was mixed with AA and $w = 2\%$

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initiator (with respect to the solvent AA), benzoin ethyl ether at room temperature (about 20 ℃). AA was distilled in vacuum at 50 ℃ before used and all of the reagents were chemically pure reagents. The mixture was allowed to sit for one or more weeks, and the resulting homogeneous solutions were then stored in the dark until used. The concentration of the (E-CE)C/AA cholesteric LC solutions was controlled in the region of 42% ~ 56%. The solutions were sandwiched between two glass slides and sealed with solid wax and stored in the dark for several hours. The thickness of solution films was controlled in 0.45 mm by a Teflon spaces. Then, the solution films were inserted into an ultraviolet chamber equipped with a 250 W high-intensity mercury arc lamp for 2 min and the (E-CE)C/PAA composites, in which the cholesteric LC order was reserved, were prepared after the polymerization of the AA. The distance between the lamp and the polymerization temperature was 0 ℃.

2.3 Measurements

The selective reflection spectra of the (E-CE)C/AA cholesteric LC solutions and the (E-CE)C/PAA cholesteric composite films were measured by an UV-VIS spectrophotometer (UV-2550, SHIMADZU, Japan). The textures and the morphology of the mesophases were observed by a transmission electron microscope (TEM) (JEM-100CX/Ⅱ, JEOL, Japan) after the sample was cut to ultra thin films by an ultra microtome (LKB-208B, BROMMA, Switzerland). The cutting direction was perpendicular to the film surface.

3 Results and discussion

When the mass fraction is above 33.8%, the cholesteric phase begins to appear in the (E-CE)C/AA solution. When the mass fraction is above 42%, 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. The pitch of the solutions is approached to the visible light wavelength and the solutions exhibit vivid colors due to the selective reflection to visible light. The maximum wavelength of the reflection of the cholesteric phase, λ_{max}, is decreased with increasing the (E-CE)C concentration (Fig.1(a)).

After photopolymerization of AA, the cholesteric order of (E-CE)C/AA solutions can be reserved in the (E-CE)C/PAA composites. From Fig.1(b), it is shown that the (E-CE)C/PAA composite also shows the selective reflection property. The relationship between the (max and the concentration in the composite is the same trend as that in the solution, that's the (max of the composites is decreased with increasing the (E-CE)C

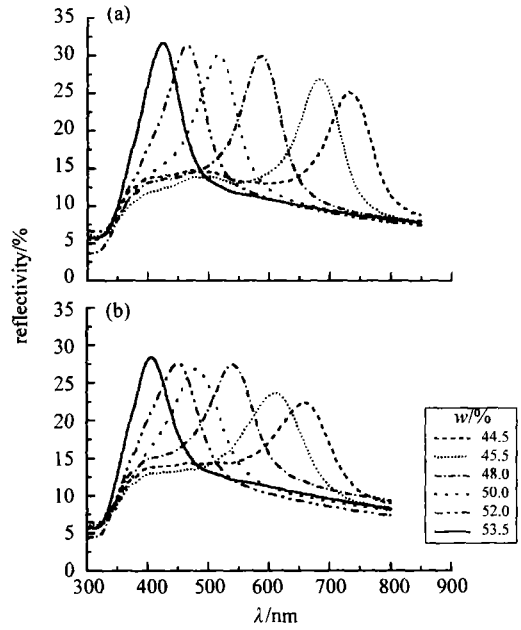

Fig.1 Selective reflection spectra of the (E-CE)C/AA cholesteric LC solutions (a) and of the (E-CE)C/PAA composites (b) *vs*. the (E-CE)C concentration

concentration. But all reflection peaks in the spectra of the composite's shift to the short wavelength direction (blue shift) compared with that of the solutions, and the selectivity and the reflectivity are decreased after the solidification of the cholesteric phase (Fig.1(b)). From the variation of λ_{max} with the concentration in Fig.1, it can be derived the relationship between the λ_{max} and the concentration of cholesteric phase in the following equation:

$$\lambda_{max} = kc^{-w} \quad (1)$$

where k, is a constant. The constant k and the exponent w for the (E-CE)C/AA solution can be calculated and they are 5.21×10^8 and 2.94, respectively. And the constant k and the exponent w for the (E-CE)C/PAA composite are 1.15×10^8 and 2.57, respectively.

It is well known that the relationship between the maximum wavelength of the reflected light λ_{max} and the pitch P and can be described by the following equation[1]:

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

where n is the average refractive index of the mesophase. After measured the average refractive index (Fig.2), the pitch of the composites is calculated according to the equation (2) (Fig.3).

It is shown that P is decreased with increasing the (E-CE)C concentration. And the result is confirmed by the observation of the transmission electron microscopy (TEM). From Fig.4, the mesophase of (E-CE)C/PAA cholesteric composites shows periodical lamellar structure, which is a typical morphology of the macromolecular

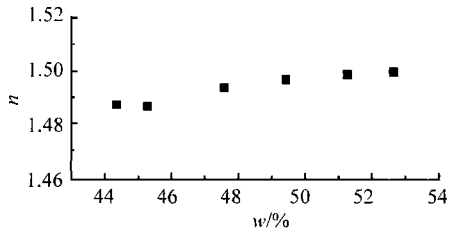

Fig.2 The average refractive index *vs*. the (E-CE)C concentration of the (E-CE)C/PAA composites

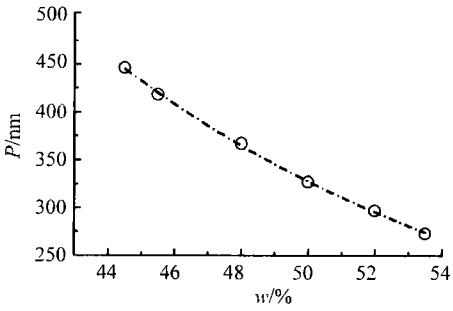

Fig.3 The pitch *P vs*. the (E-CE)C concentration of the (E-CE)C/PAA composites

cholesteric phase and reflects the periodical variation of the molecular orientation in the cholesteric phase[20]. The periodicity of the periodical lamellar structure coincides with the half pitch ($P/2$). It shows that the pitch is decrease with increasing the concentration.

4 Conclusion

After photopolymerization of AA, the structure and the selective reflection property of the (E-CE)C/AA solutions is retained in the (E-CE)C/PAA composites. The wavelength of the reflection and the pitch are decreased with increasing the (E-CE)C concentration and can be controlled precisely.

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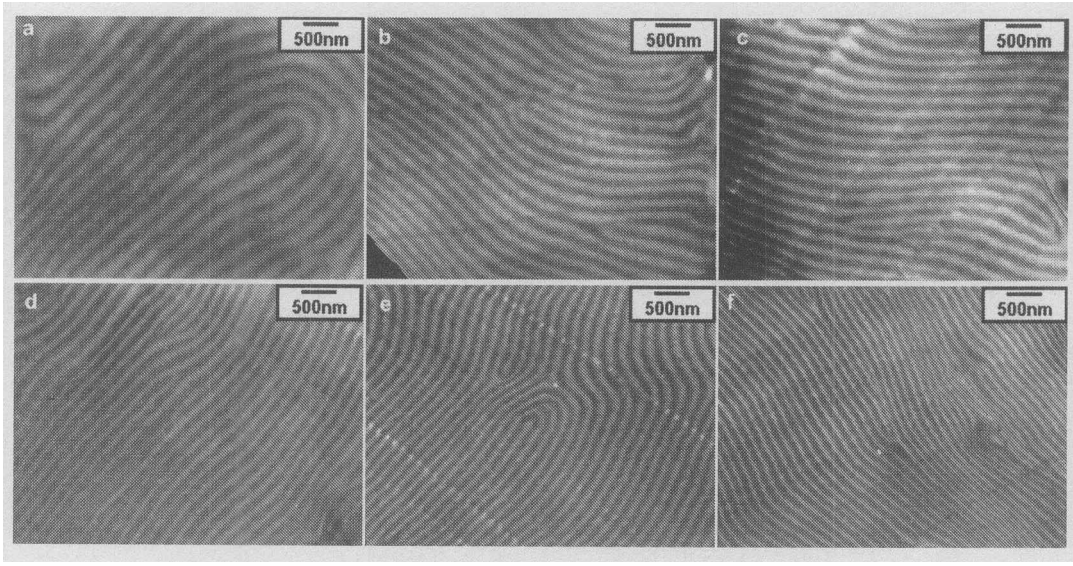

Fig.4 TEM micrographs of the cholesteric structure of the (E-CE)C/PAA composites
***w*/%**: (**a**) 44.5, (**b**) 45.5, (**c**) 48.0, (**d**) 50.0, (**e**) 52.0, (**f**) 53.5

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乙基氰乙基纤维素/聚丙烯酸复合物膜结构和光学性能

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摘 要:乙基氰乙基纤维素[(E-CE)C]可溶解在丙烯酸(AA)中形成胆甾相液晶,通过光聚合 AA,原胆甾相结构可以被"固定"在(E-CE)C/聚丙烯酸(PAA)复合物中,其结构和选择性反射光性能通过电镜和紫外-可见光光谱进行了研究。研究表明该复合物膜的反射光波长和浓度呈指数关系,反射光强度与膜厚有一定关系,并在低于160 ℃时有很好的热稳定性。

关键词:乙基氰乙基纤维素;高分子液晶;光聚合;复合物
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