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TEM observation of (E-CE)/PAA composite polymerized by ultraviolet initiation

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ABSTRACT

From the ethyl-cyanoethyl cellulose((E-CE)C)/acrylic acid(AA) solution, the (E-CE)C/PAA composite can be prepared by polymerizing the AA with ultraviolet initiation. The (E-CE)C/PAA composite prepared from the cholesteric liquid crystalline solution shows the lamellar structure with a periodicity ranging from 400 to 600 nm. In the lamellation there is no preferential orientation direction for polymer chains. The PAA is dispersed between the lamellea with small strip-like domains and the PAA and (E-CE)C have been homogeneously mixed in the system.

INTRODUCTION

Electron microscopy investigations have provided much of the information on general polymer morphology[1]. Thomas et al[2] have studied the texture and defects in the thermotropic liquid crystalline polymer with lower melting flexible spacer by using transmission electron microscopy(TEM). They have found that the crystalline morphology and structure of thermotropic liquid crystalline polymers is related with the mesophase texture and defects before polymerization. Liquid crystals can not be directly observed by a electron microscope because of their fluidity. Lyotropic liquid crystals are destroyed by evaporation of the solvent. Under specific conditions, however, solid state can retain a helicoidal organization for cholesteric mesophase system. Classical embedding and ultra-sectioning can thus be applied on such materials as long as they do not dissolve in water and electron microscopy can be used in study. It has been known that in some synthetic polypeptide/vinyl monomer and cellulose/vinyl monomer systems, the cholesteric liquid crystalline state can be immobilized by polymerizing the solvent[3-7].

Cellulose and many of its derivatives can form liquid crystals because of their semirigid backbone[8]. Ethyl-cyanoethyl cellulose ((E-CE)C) can be dissolved in many organic solvents and formed liquid crystalline solution[9]. In acrylic acid(AA), the (E-CE)C can form cholesteric mesophase when the concentration is above the critical value and the (E-CE)C/PAA composite can be prepared by polymerizing the AA[10]. In this report, the morphology and structure of the (E-CE)C/PAA composite prepared from the liquid crystalline solution is studied by electron microscopy.

EXPERIMENTAL

(E-CE)C was obtained by reacting ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile. The degree of substitution for ethyl cellulose was about 2.1 and for cyanoethyl was about 0.43 as determined by elementary analysis. The degree of polymerization was about 280. AA was a chemically pure reagent and distilled at 50°C under reduced presure before used.

The (E-CE)C was mixed with the AA at room temperature and the solution was sandwiched between two quartz slides to form a solution film about 0.5-1.0 mm in thickness after it was stored at room temperature for one week. The edges of the slides were sealed with solid wax and allowed to sit for two days, and then inserted into the UV chamber until completely polymerized. The Ultraviolet initiation was carried out with 2% (related with the AA) diphenyl ketone as initiator and 0.5% N,N-dimethylaniline as promoter. The ultraviolet source was a 250 watt high intensity mercury arc lamp and the distance between the UV source and the specimen was 3 cm. The (E-CE)C/AA solutions were polymerized 2 minutes to achieve virtually total monomer utilization.

The (E-CE)C/PAA composite plate was sectioned in the direction normal and parallel to the plate surface after it was embedded with epoxy. A transmission electron microscope (JEOL 100 CX-II) was used to examine the specimen.

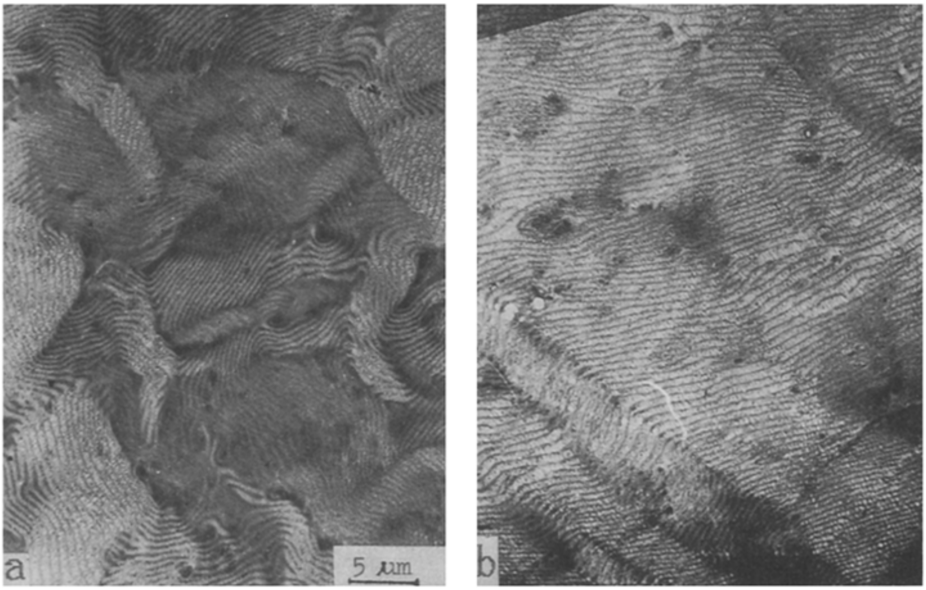

Fig.1 TEM micrographs of the (E-CE)C/PAA composite with 40% (E-CE)C, section (a) parallel and (b) normal to the composite plate surface.

RESULTS AND DISCUSSION

The (E-CE)C/AA solution is isotropic when the concentration is under 33.0 wt% and mesophase appears in the solution at the concentration above 33.0 wt%. The (E-CE)C/AA solution with concentration of 20, 35 and 40 wt% is used to prepare the (E-CE)C/PAA composite with 20, 35 and 40% (E-CE)C, respectively. Fig.1 shows two different sections of the (E-CE)C/PAA composite with 40% (E-CE)C. In Fig.1a, the section is parallel to the composite plate surface, where it is perpendicular in Fig.1b. It can be clearly observed in Fig.1 that there is a well-difined high contrast lamellation with periodicity ranging from 400 to 600 nm. These lamellar structure zones probably correspond to the areas where the lamellea are almost normal to the observation plane. Other regions with lower contrast and broader spacings may correspond to the areas where the lamellea are viewed obliquely. Sections of the composite with 35% (E-CE)C exhibit the same type of the structure as those of the composite with 40% (E-CE)C.

When the concentration is 20 wt%, the (E-CE)C/AA solution is isotropic and in the composite with 20% (E-CE)C, the electron micrograph shows a complete absence of the periodical lamellar structure, which means that no periodical structure exists in the composite prepared from the isotropic solution and the periodical lamellation can exist in the composite only if the polymerization of the AA is initiated in cholesteric liquid crystalline state. Giasson et al[11] have observed the cellulose triacetate film cast from the cholesteric mesomorphic solution and found the existance of the periodical lamellation. We have studied the cyanoethyl cellulose film prepared from the cholesteric liquid crystalline solution with TEM and also observed the lamellar structure similar to that in Fig.1 and moreover, the lamellar structure can only be observed in the film cast from the mesomorphic solution but the isotropic one. It is considered, therefore, that the periodical lamellation shown in Fig.1 is closely related with the helicoidal arrangement characteristic of cholesteric mesophase existing in the solution before polymerization.

After polymer liquid crystals are sheared, the band-like texture is generally observed by polarizing microscopy. In the band-like texture, the band direction is normal to the shearing direction and polymer chains orient in the shearing direction[12]. In the (E-CE)C/PAA composite, some of the periodical lamellation seems similar to the band-like texture and especially in the section normal to the composite plate surface, the lamellea arrange in the same direction in a big area. In this region,

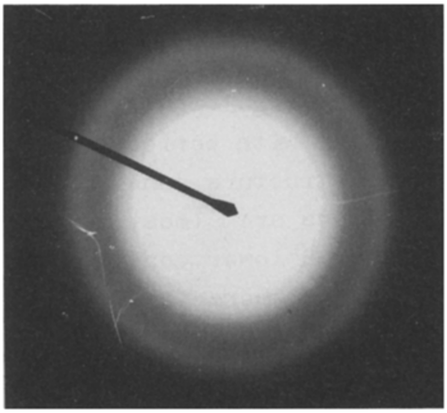

Fig.2 Electron diffraction pattern of the (E-CE)C/PAA composite with 40% (E-CE)C, section normal to the composite plate surface.

however, the electron diffraction pattern(Fig.2) shows that polymer chains have no preferential orientation direction. The electron diffraction pattern is a dispersed ring, which reflects that the composite is amorphous and unoriented although there is the periodical lamellar structure in it. The large angle X-ray diffraction also shows that the (E-CE)C/PAA composite is almost an amorphous system. These results indirectly indicate that the periodical lamellar structure in the composite is related with the existance of cholesteric mesophase in the solution before the polymerization of the AA. In the cholesteric mesophase, polymer chains arrange to layers and in each layer polymer chains orient in the same direction but the orientation direction is different between the layers of ordered polymer chains. And consequently, there is no preferential orientation direction for polymer chains in cholesteric helicoids(Fig.3). The helicoidal arrangement characteristic of cholesteric mesophase can not be changed in the polymerization because the viscosity of the concentrated (E-CE)C/AA solution is high and the AA is polymerized very fast. The (E-CE)C/PAA composite prepared from the cholesteric mesomorphic solution, therefore, retains the characteristic of cholesteric helical structure formed before polymerization and consequently, polymer chains have no preferential orientation direction in the composite.

The physical basis for periodicity in the electron micrograph

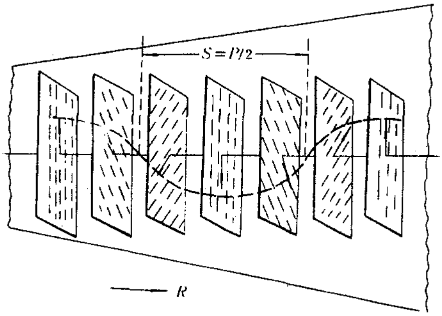

Fig.3 The scheme of helicoidal supermolecular arrangement in cholesteric mesophase.

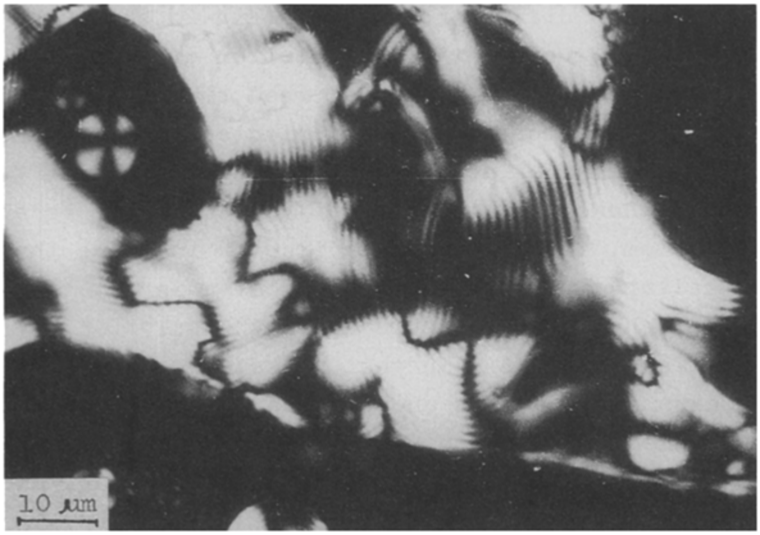

Fig.4 Polarizing micrograph of the (E-CE)C/DCA liquid crystalline solution, C=28.6 wt%.

of cholesteric structure is not clear. The cholesteric helical structure is highly anisotropic in optics. When the (E-CE)C forms cholesteric mesophase, the fringeprint structure(Fig.4), which is similar to the image in Fig.1, can be observed with polarizing microscopy[13]. The fringeprint structure results from the periodicity in refractive index normal to the axis of the helicoidal cholesteric arrangement. Electron is wave-particle duality in transmitting. It is possible that the helicoidal cholesteric arrangement is also anisotropic in electron transmitting and the speed of electron transmission is different in the directions between parallel and perpendicular to the orientation direction of polymer chains. In these different parts of the specimen, therefore, the density of the transmitted electon is different. Like with the optical microscopy, the typical texture of cholesteric mesophase can also be observed with the TEM becuase the orientation direction of polymer chains in helicoidal cholesteric arrangement is different between the layers of ordered polymer chains. From the selective reflection of cholesteric mesophase, it can be known that the pitch of helicoids in the 40 wt% (E-CE)C/AA solution is about 450-550 nm,

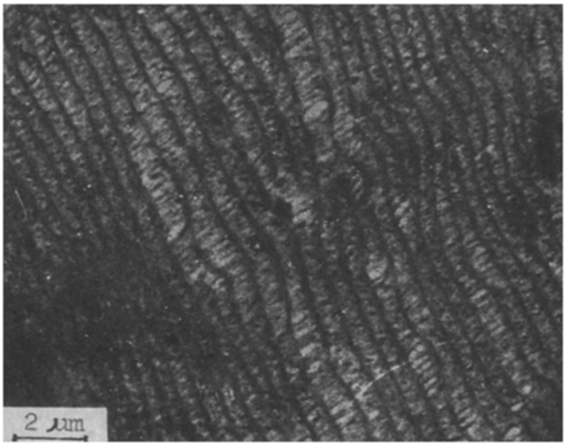

Fig.5 Electron micrograph of the composite with 40% (E-CE)C. section perpendicular to the composite plate surface.

Which is almost the same as the width of the lamellea in the composite with 40% (E-CE)C observed by TEM. Therefore, the width of the lamellation is equal to a half pitch.

Fig.5 shows the details of the periodical lamellar structure in the section of the composite with 40% (E-CE)C. The small strip-like domains can be observed between the lamellea. The width of these domains is about 100-200 nm and they arrange perpendicularly to the lamellea. These domains are probably PAA microphase in the composite. Before polymerization, the AA, as a solvent, is dispersed between the layers of ordered polymer chains and betwwen the ordered helicoids. The AA molecules move difficultly when polymerized because of the high viscosity of the system and the high rate of the polymerization. In the composite, therefore, the PAA microphase is dispersed homogeneously in the system with the small domains. While, there is obvious phase separation between (E-CE)C and PAA in the composite with 20% (E-CE)C.

CONCLUSIONS

The morphology and structure of the (E-CE)C/PAA composite depends on the (E-CE)C/AA solution state before polymerization. The composite prepared from the cholesteric mesomorphic solution retains the helicoidal arrangement characteristic and shows the periodical lamellation although it is amorphous. In the periodical lamellation, polymer chains do not orient in one direction, i.e. there is no preferential orientation direction for polymer chains. The helicoidal arrangement characteristic is freezen in the composite during polymerization. The PAA microphase is homogeneously distributed between the lamellea with the strip-like domains. The mixture state of (E-CE)C and PAA is homogeneous by polymerizing the AA in the (E-CE)C/AA liquid crystalline solution although the compatibility of them is poor.

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