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Atomic force microscopy on ethyl–cyanoethyl cellulose/polyacrylic acid composites with cholesteric order

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Ultra-thin slices of ethyl–cyanoethyl cellulose [(E–CE)C]/polyacrylic acid [PAA] composites with cholesteric order were prepared by ultra-microtoming and observed by atomic force microscopy (AFM). The morphology of a periodic lamellar structure in the composites with cholesteric order was revealed, which was induced by the twist of the molecular orientation in the cholesteric phase, and it reflected the structural features of the cholesteric phase in the systems. It was found that microphase separation appears even when the composites are prepared by photopolymerization, and the dimensions of the microphases are generally smaller than 200 nm. The structural features of the cholesteric phase were not influenced by the microphase separation.

(Keywords: AFM; cholesteric order; lamellar structure)

INTRODUCTION

Macromolecular cholesteric liquid crystals are of great interest in basic research because most of the biopolymers, such as polypeptides, DNA, RNA and so on, can form cholesteric lyotropic liquid crystals[1]. Until now, however, the structure and the orientational arrangement of polymer chains in the cholesteric liquid crystals have not been well understood. There are only a few synthetic polymers which can form the main-chain cholesteric liquid crystalline state. The methods of investigating structures of lyotropic liquid crystals are generally restricted to optical microscopy, d.s.c. and X-ray diffraction, by which it is difficult to reveal the structure in the scale from 10 nm to 1 μm. Thus, investigations with electron microscopy on the morphology and structure of the macromolecular cholesteric liquid crystals have been carried out in the last few years[2–4]. The periodic lamellar structure in the cholesteric phase has been observed by transmission electron microscopy (TEM). However, the correlation between the lamellar structure and the cholesteric order is not very clear because until now the reason for the contrast in the TEM observations of the material with cholesteric order has been under debate. Recent developments in scanning probe techniques[5] offer the possibility of direct investigations of solid surfaces from the micro scale to the molecular scale. The atomic force microscope (AFM) is one of these kinds of instruments, and it is thus promising that the AFM may yield new insights into the morphology and structure of the macromolecular cholesteric liquid crystals.

Cellulose and most of its derivatives can form lyotropic liquid crystals in the appropriate solvents because of their semirigid backbone, and some cellulose derivatives can also form thermotropic liquid crystals[6]. The liquid crystals formed from cellulose and its derivatives are generally cholesteric. In the lyotropic polymer liquid crystals with a monomer as the solvent, liquid crystalline polymer/thermoplastics composites can be prepared, if the solvent is polymerized in the liquid crystalline solution, and the liquid crystalline structure in the solution may be conserved in the composite[7,8].

Ethyl–cyanoethyl cellulose [(E–CE)C] can be dissolved in acrylic acid [AA] and forms cholesteric liquid crystalline solutions[9]. The AA can be polymerized in the cholesteric liquid crystalline solutions and (E–CE)C/polyacrylic acid [PAA] composites with cholesteric order can be prepared[10]. The periodic lamellar structure in the (E–CE)C/PAA composites with cholesteric order has been observed by TEM. In this paper, ultra-thin slices of the (E–CE)C/PAA composite films with cholesteric order are examined by AFM and the correlation of the lamellar structure and the cholesteric order is discussed.

EXPERIMENTAL

The (E–CE)C was prepared by the reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.43. The molecular weight of the (E–CE)C, M_n, measured by gel permeation chromatography (g.p.c.) (h.p.l.c., Waters ALC/244/GPC) and calibrated by standard polystyrene, was about 70 000. The molecular formula of the (E–CE)C is shown in *Figure 1*. The AA was a chemically pure reagent and was distilled before use. Other chemicals were chemically pure reagents and used without additional purification.

(E–CE)C/AA solutions were prepared in glass vials by mixing (E–CE)C, AA and initiator (benzoin ethyl ether) at room temperature. The mixtures were allowed to sit for one or more weeks, and the resulting homogeneous solutions were then stored in the dark until use. The photopolymerization of the cholesteric liquid crystalline solution films with a thickness of about 0.3 mm was carried out by

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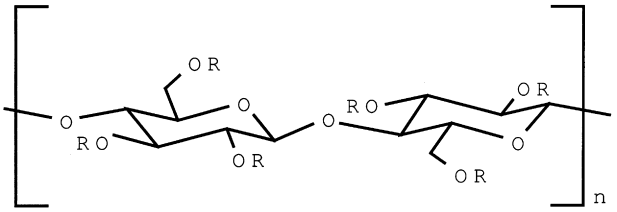


R = H, CH_2CH_3, CH_2CH_2CN

Figure 1 Molecular formula of ethyl–cyanoethyl cellulose

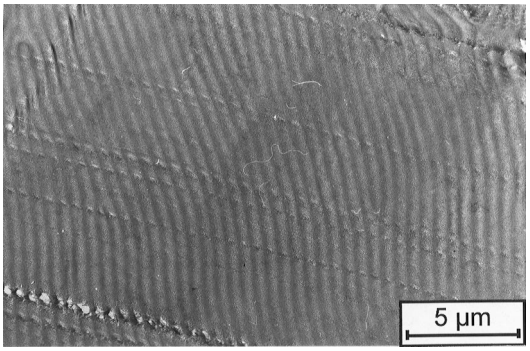


Figure 2 TEM micrograph of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at 0°C

inserting the samples into an ultraviolet chamber with a 250 W high-intensity mercury arc lamp until polymerization was complete. The distance between the lamp and the sample was about 3 cm and it took about 20 s to several minutes for complete polymerization.

The (E–CE)C/PAA composites were sectioned into ultra-thin slices by an ultra-microtome (REICHERT ULTRA-CUT S, Leica, Germany) at room temperature and − 60°C. In the AFM investigations, the slices were loaded onto copper grids and fixed on the sample stage. AFM measurements were carried out in contact mode with an Atomic Force Microscope (Rasterscopeth 3000, DME—Danish Micro Engineering A/S, Denmark). The cantilevers used were as supplied by the microscope manufacturer and had a theoretical force constant of 0.01–0.4 m^{-1}.

The AFM micrographs are presented as top-view or three-dimensional images. No filtering was used, so that all the images were reproduced in the same quality as they were acquired.

RESULTS AND DISCUSSION

Earlier TEM observations of ultra-thin composite slices, sectioned by an ultra-microtome, showed the lamellar structure with the periodicity of about 400–600 nm (*Figure 2*)[4], and some sub-structures in the composite films were also observed. The periodicity of the lamellar structure in the composite films coincides with the half pitch of the cholesteric phase in the solution before polymerization[10]. Thus, it is assumed that the periodic lamellar structure reflects the structural features of the macromolecular cholesteric phase.

Figure 3 shows a 9 × 9 μm^2 AFM surface image of a composite film. The periodic lamellar structure can be clearly observed and the lamellae cross the image from the upper left corner to the lower right corner. As measured from the image, the width of the lamellae is about 420 nm and the height of the lamellae (the value from local peak to valley) is about 30 nm. *Figure 3* indicates the morphology

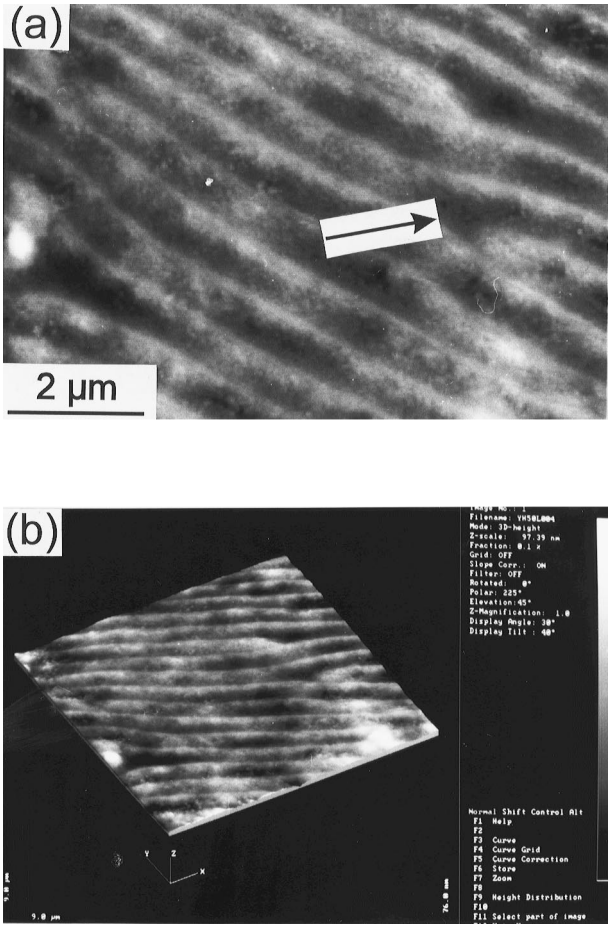


Figure 3 AFM micrographs of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at − 10°C: (a) two dimensional image and (b) three dimensional image

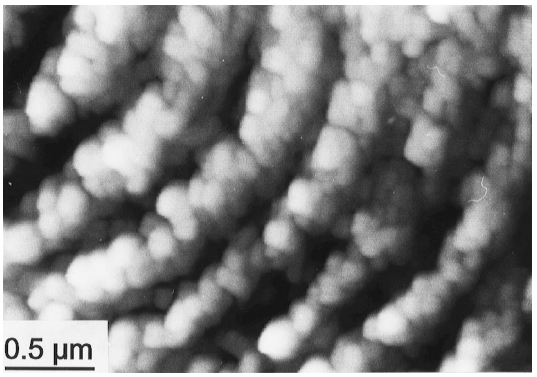


Figure 4 AFM micrographs of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at 30°C

of the surface of the ultra-thin composite slices and it can be seen that the height of the slices varies periodically.

The width of the lamellae in the composites, observed by AFM, is almost the same as that observed by TEM. Consequently, the periodic lamellar structure in the composites, observed by both TEM and AFM, presents the same morphology of the ultra-thin slices of the composites with cholesteric order. The AFM observations indicate that the surface of the ultra-thin slices is not smooth. It is suggested that the morphology of the lamellar structure in the ultra-thin slices may be created by the deformation of the composites, when they are sectioned by ultra-microtoming.

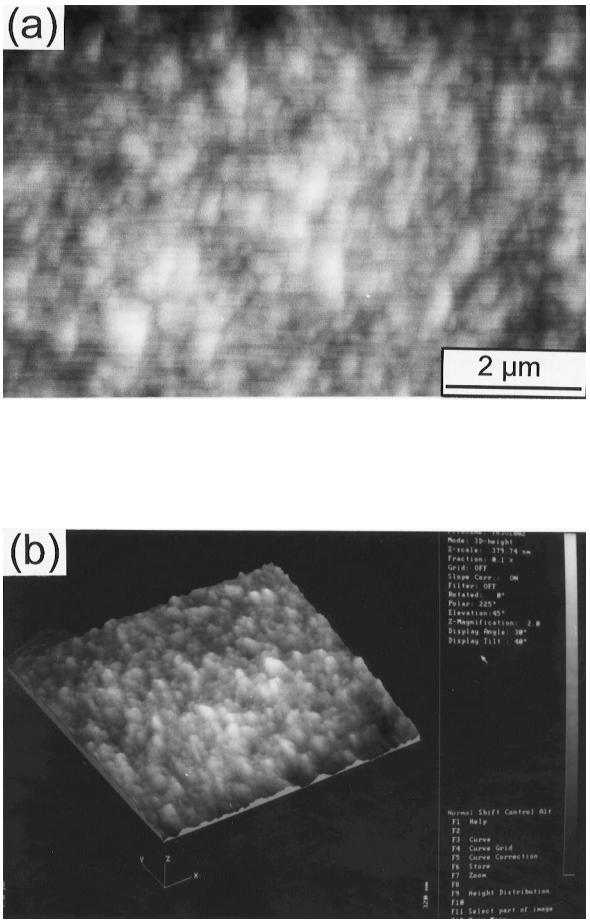


Figure 5 AFM micrographs of the (E–CE)C/PAA composite prepared from the isotropic solution (30 wt%) at 0°C: (a) two dimensional image and (b) three dimensional image

The direction of the lamellae in the ultra-thin slices is independent of the cutting direction. It can be observed in *Figure 4* that the direction of the lamellae gradually changes, and in this area, they look like a part of a concentric ring morphology. Slices with varying thickness were also examined by AFM and it was found that the slices with different thicknesses exhibit the same morphology, which means that the existence of the lamellar structure in the ultra-thin slices is not influenced by the preparation conditions. Furthermore, the slices, which are sectioned at room temperature and −60°C, also show the same morphology of the lamellar structure by the AFM observations. The results indicate that the appearance of the lamellar structure is independent of the sectioning conditions. Consequently, if the lamellar structure in the ultra-thin slices is created by the deformation when the composites are sectioned with a microtome, this deformation must be dependent on the direction of the molecular orientation in the cholesteric phase. It is assumed that the deformation of the layers, in which the molecular orientation is normal to the cutting direction, is different from those where the molecular orientation is parallel to the cutting direction. Consequently, the deformation mode must be changed with the variation of the molecular orientation direction in the cholesteric phase.

The morphology of the composites with isotropic structure is significantly different from those with cholesteric order. *Figure 5* shows the surface morphology of an ultra-thin slice of the composite containing isotropic

Table 1 The values of the width (*WL*) and the height (*HL*) of the lamellae in (E–CE)C/PAA composites with cholesteric order

Polymerization temperature (°C)	−10	0	0	30
(E–CE)C composition (wt%)	50	42	50	50
WL (nm)	417	349	387	315
HL (nm)	31	65	38	60

structure. No periodic lamellar structure can be observed in *Figure 5* and it implies that the morphology of the periodic lamellar structure is only typical for the composite with cholesteric structure. Therefore, appearance of the lamellar structure in the ultra-thin slices is dependent on the structure of the composites.

Cholesteric liquid crystals are also called twisted nematic liquid crystals and the structure of the cholesteric phase acquires a spontaneous twist of the molecular orientation around an axis perpendicular to the director. When (E–CE)C/PAA composites with cholesteric order are sectioned by an ultra-microtome, the sectioning of the molecular chains in the cholesteric phase is heterogeneous because of the twist organization. The deformation in a local area, in which the molecular orientation is normal to the edge, is supposed to be different from that in which the molecular orientation is parallel to the edge. It is presumed that there is maximum deformation when the molecular orientation is normal to the edge and minimum deformation when the molecular orientation is parallel to the edge. Consequently, the degree of the deformation will continuously change when the molecular orientation direction is changed from normal to the edge to parallel to it. *Figure 6* schematically demonstrates the variation of the deformation with the direction of molecular orientation in the cholesteric phase. The peak has the maximum deformation and the valley has the minimum deformation in the lamellar structure. So, the periodic lamellar structure is actually attributed to the twist of the molecular orientation direction.

Some defects in the lamellar structure, which have been observed by TEM[12], can also be observed by AFM. In *Figure 7*, there is a disclination with the strength $S = -1/2$. Some kinds of pairs of disclinations can also be seen in the AFM micrographs (*Figure 3*, indicated by arrows). All these defects have also been observed in the cholesteric liquid crystalline solutions by polarizing microscopy. These results confirm that the periodic lamellar structure reflects the structural features of the macromolecular cholesteric liquid crystals.

The lamellar structure should vary with the variation of the volume fraction of the components in the composites, if it reflects the structural features of the composites with cholesteric order. The structure of the composites is dependent on their preparation conditions, such as the concentration of the solution before polymerization and the polymerization temperature[11]. It has been found in the AFM images that the width and the height of the lamellae are mainly dependent on the preparation conditions of the composites. *Table 1* gives the values of the width (*WL*) and the height (*HL*) of the lamellae in the composites having different compositions and different polymerization temperatures. The data in *Table 1* shows that the width of the lamellae increases but their height decreases with decreasing polymerization temperature. If the concentration of the solution before polymerization is higher, the width of the lamellae is larger but their height is smaller. The degree of

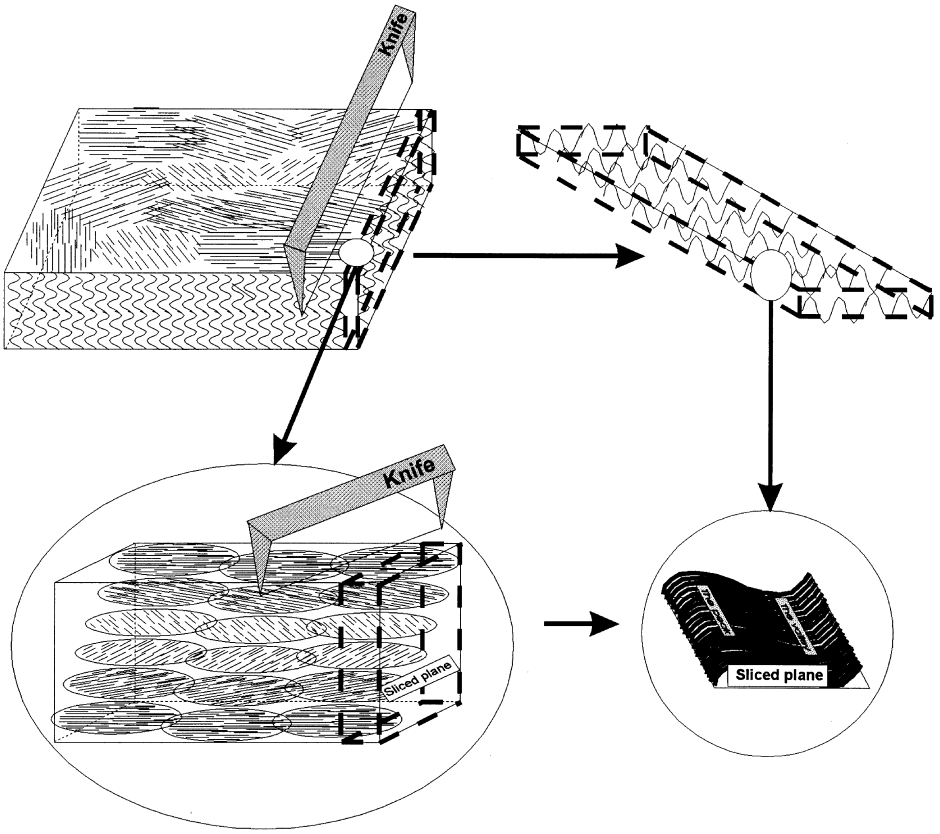


Figure 6 Scheme of the variation of the deformation with the molecular orientation direction in the cholesteric phase

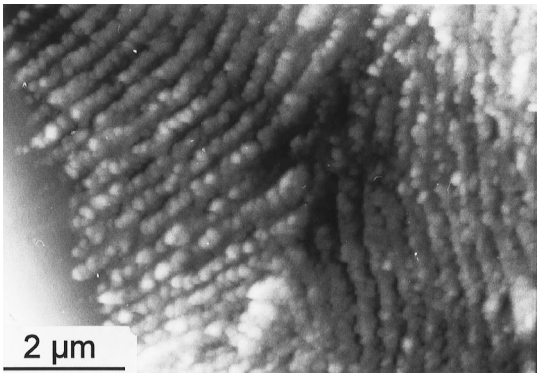
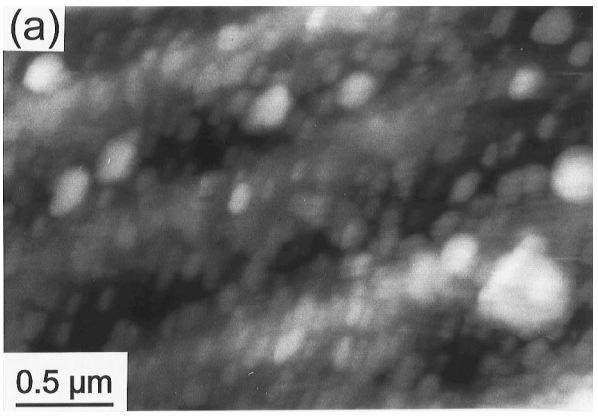


Figure 7 AFM micrographs of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at 30°C

the deformation, when the composites are sectioned by an ultra-microtome, may be reflected by the height of the lamellae. The larger deformation may result in higher lamellae. Consequently, it can be seen from *Table 1* that the degree of the deformation is influenced by the concentration of the solution before polymerization and the polymerization temperature. As is known[11], the higher the concentration of the solution before polymerization and the lower the polymerization temperature, the better the cholesteric order is conserved in the composites. Therefore, the deformation of the composites is dependent on the degree of cholesteric order in the composites. The variation of the lamellae with the preparation conditions demonstrates again that the morphology of the lamellar structure reflects the structural features of the cholesteric phase in the composites.

In the AFM images, many small particles are found in the lamellar structure. It can be observed in *Figure 7* that the



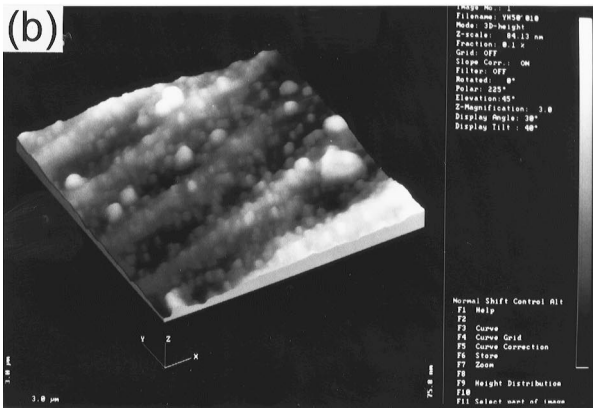


Figure 8 AFM micrographs of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at −10°C: (a) two dimensional image and (b) three dimensional image

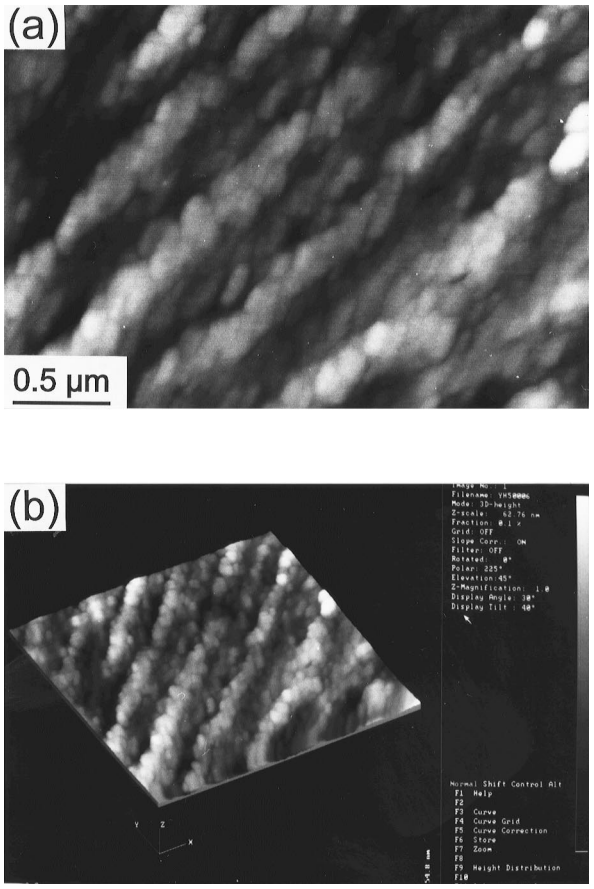


Figure 9 AFM micrographs of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at 0°C: (a) two dimensional image and (b) three dimensional image

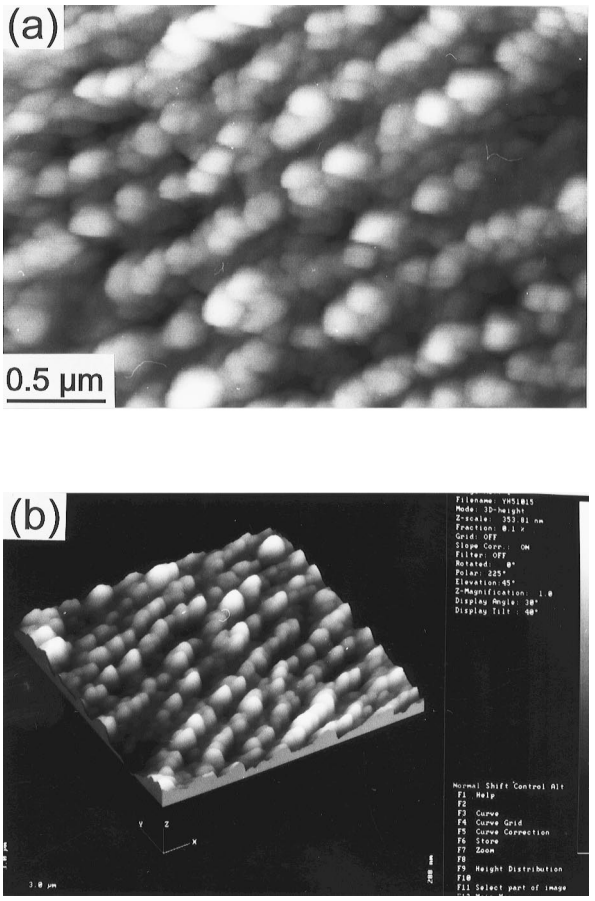


Figure 10 AFM micrographs of the (E–CE)C/PAA composite prepared from the cholesteric liquid crystalline solution (50 wt%) at 30°C: (a) two dimensional image and (b) three dimensional image

Table 2 The values of the dimension (*DP*) and the height (*HP*) of the-particles in (E–CE)C/PAA composites with cholesteric order observedby AFM

Polymerization temperature (°C)	−10	0	0	30
(E–CE)C composition (wt%)	50	42	50	50
DP (nm)	99	213	163	182
HP (nm)	4.4	23.4	8.6	39.7

lamellar structure is composed of these small particles. The dimension of these particles is generally smaller than 200 nm. The (E–CE)C/PAA composites prepared by photopolymerization show a single T_g, measured by d.s.c., which implies that the composites are homogeneous within the d.s.c. resolution and no phase separation occurs[10]. The AFM images, however, demonstrate that a microphase separation may have occurred even when the composites were prepared by photopolymerization. The microphase separation may not be reflected by T_g measurements, because the dimension of the microphase is too small. But the microphase separation obviously does not change the structural features of the cholesteric phase in the composites.

Figures 8–10 are AFM images of the composites, prepared at different temperatures. It is found that the dimensions and the heights of the particles vary with the variation of the temperature at which the composite is prepared. The dimension of the particles reflects the degree of the microphase separation and the height of the particles reflects the deformation of the composites. *Table 2* gives the dimension (*DP*) and the height (*HP*) of the particles in the composites, prepared under different conditions. It is found that the variation of the dimension and height of the particles is similar to that of the width and height of the lamellae. Both the dimension and height of the particles decrease with increase of the concentration of the solution before polymerization and decrease of the polymerization temperature, which means that the degree of the microphase separation and the deformation decrease with both increase of the concentration of the solution before polymerization and decrease of the polymerization temperature. The cholesteric order would be destroyed by macroscopic phase separation during the polymerization[10]. Therefore, the cholesteric order is preserved to a large extent in the composites, if the phase separation can be kept on a microscale during the polymerization.

CONCLUSIONS

A periodic lamellar order is observed in the (E–CE)C/PAA composites containing cholesteric order. The periodic lamellar structure observed by AFM reflects the structural features of the macromolecular cholesteric liquid crystals but is created by the cutting of the ultra-thin slices during preparation. A microphase separation appears even when the composites are prepared by rapid photopolymerization. The dimensions of the microphase are smaller than 200 nm, but the cholesteric order is not changed by the microphase separation.

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