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Evidence for cholesteric morphology in films of cellulose acetate butyrate by transmission electron microscopy

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Summary

Transmission electron microscopy provides direct evidence of helicoidal cholesteric morphology in films of cellulose acetate butyrate prepared by solvent casting from liquid crystalline solutions in dimethylacetamide. We believe this is the first observation reported of cholesteric structure in a mixed cellulosic ester. Cholesteric morphology was also observed in solvent cast blended films of cellulose acetate butyrate and lignin from liquid crystalline solutions. There are indications that lignin particles may be serving as nucleating surfaces or sites of direct termination for some of the observed cholesteric fingerprint pattern.

Introduction

Extensive attempts have been made to prepare polymeric films with cholesteric order by different techniques (1-3).

Since the first observation of cholesteric liquid crystalline textures in a solution of hydroxypropyl cellulose [HPC] (4), the field of cellulosic liquid crystals has expanded rapidly, and there have been numerous reports of lyotropic and thermotropic liquid crystalline systems with cellulose and its derivatives (5-7). The semi-rigid character of the cellulose backbone is responsible for the development of mesophases in these materials (8). Besides scientific pursuit, one primary motivation to study cellulosic liquid crystalline systems has been the potential of industrially preparing high strength/ high modulus regenerated fibers.

In this paper, we present the first evidence for the cholesteric structure in films of cellulose acetate butyrate (CAB), and in blended films of CAB and lignin prepared from liquid crystalline solutions by transmission electron microscopy (TEM).

Experimental

I. Materials.

Cellulose acetate butyrate (CAB 500-5) was obtained from Eastman Kodak, Kingsport, TN. The degree of substitution (DS) of acetyl (DS_{AC}) and butyryl (DS_{BU}) groups was 0.29 and 2.57, respectively. The value of DS_{OH} was determined by difference [$DS_{OH} = 3 - \{0.29 + 2.57\} = 0.14$]. Number average molecular weight ($<M_n>$), polydispersity, and intrinsic viscosity (I.V.) were 52,600 gm/mole, 2.4, and 1.51 dL/g, respectively.

Unmodified organosolv lignin was supplied by Aldrich Chemical (Cat. No. 37,101-7). Its $<M_n>$, polydispersity, and I.V. were 800 gm/mole, 4.4, and 0.05 dL/gm, respectively.

Reagent grade dimethylacetamide (DMAc) was used as received.

II. Methods:

1. Film Preparation:

Since we have found by rheological investigations that this particular CAB behaves

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as a liquid crystalline solution in DMAc above 35% (w/w) concentration (9). Hence, in the present study, the total solids content in all the solutions was maintained at a constant value of 40% (w/w) and the lignin content varied from 0 to 20% (w/w) of organic solutes. Individual component solutions made from dried CAB and lignin were prepared in DMAc. These were mechanically mixed for 12 hours at ambient temperature to prepare blended liquid crystalline solutions. The solutions were allowed to equilibrate for 1 week.

Portions of the viscous solutions were poured on to Teflon molds and a glass rod was very gently pushed over the solutions to form thin films to minimize any significant shearing. Films from sheared solutions were prepared by rapidly applying a unidirectional force using a glass slide. The molds were covered by glass plates and the solvent was allowed to evaporate at ambient conditions for 5 days. The resulting solid films were removed from the molds, and dried in a vacuum oven at 60°C for 48 hours to remove residual solvent. Amorphous films were prepared by heating the dried films in a hot press and quenching them from the melt state.

2. Polarized Optical Microscopy:

The films were observed between cross polarizers for birefringence with a Zeiss Axioskop Microscope at room temperature.

3. Transmission Electron Microscopy:

Films were embedded in Poly/Bed 812 (Polysciences, Inc.) cured at 60°C for 48 hours in flat molds. 80-90 nm thick sections were cut across the cross-section and longitudinal-section from the embedded films with a diamond knife mounted on a Reichert Ultracut E microtome. Care was taken to cut sections from different layers of the films. All the cut sections were mounted on copper grids. In some cases, staining was carried out for 30 minutes by exposing some of the copper grids to vapors of 0.5% stabilized aqueous solution of ruthenium tetroxide (RuO_4) (Polysciences, Inc.) in a small thin layer chromatography container. The copper grids were observed on a JEOL JEM-100CX-II electron microscope operated at an accelerating voltage of 80 kV. All the micrographs were bright field images of the cut sections.

Results and Discussion

Figure 1 shows the optical micrograph of the CAB film containing 20% (w/w) lignin observed between cross polarizers. There are indications of molecular orientations similar to helicoidal arrangements characteristic of cholesteric liquid crystals. Since the cholesteric pitch is equal to or shorter than 1 μm, it is difficult to define the features of the pattern with visible light. Therefore, further evidence for cholesteric morphology was obtained by electron microscopy.

Freeze-fractured surfaces of the same film were observed by scanning electron microscopy (SEM), but there was no clear indication of any structural layering. Similar difficulty in obtaining useful structural detail by SEM was also encountered by Hara et al. (10) for cholesteric mesophases of thermotropic copolyesters.

Figure 2 (a) shows the TEM micrograph of the unstained cross-section of the same film. A well-ordered cholesteric arrangement is revealed with a periodicity ranging from 500-900 nm which is in good correspondence with the optical microscopy observations. Films cut in the longitudinal-section showed analogous patterns. Similar cholesteric morphology was also seen in the CAB films without lignin. However, the cholesteric structure seemed to be distinctly more pronounced in the presence of lignin. It is not surprising to observe the twisted cholesteric order in the CAB films as comparable observations have been made by

TEM for solvent cast films from nonlignin containing liquid crystalline solutions of cellulose acetate [CA] and cellulose triacetate [CTA] (11). However, their structures were more tightly arranged with a periodicity of about 25-45 nm. The bulky butyryl side-chain substituent in the CAB moiety may prevent this system from organizing in as compact a manner, and this may eventually lead to a wider periodicity between the striation lines. TEM observations of the sheared films did not exhibit the mesophase structure. We believe this is due to the permanent disruption of the cholesteric structure by shearing and thermal treatment.

The cholesteric structures of thermotropic copolyesters exhibited in the study of Hara et al. (10) are comparable to those reported in this paper. They determined the cholesteric pitches (200-500 nm) by circular dichroism (CD) and reflection spectra which correlated well with their TEM observations. CD measurements were not conducted in our study as these measurements made by Giasson et al. (11) could not indicate the pitch of the cholesteric structure in CA and CTA films.

While Giasson et al. (11) had no explanation for the cholesteric structures observed in their study, Hara et al. (10) interpreted their structures to represent typical disclinations ($+\pi$ and-π) and translation dislocations. In our study, $+\pi$ disclinations (mostly λ^{+}-type) were observed more frequently than -π disclinations (mostly λ^{-}-type). Translation dislocations (mostly $\tau^{-}\lambda^{+}$) were also observed occasionally. The cholesteric liquid crystalline texture we observe is believed to be represented by well-defined twisted structures. This type of pattern exhibits certain regularity in electron density which corresponds to the helicoidal supramolecular organization typical of a cholesteric mesophase. In regions with highest contrast, a near regular spacing is observed as the lines are arranged perpendicular to the electron beam. However, in regions with lower contrast, a broad or irregular spacing is noticed as the lines are obliquely organized to the incident electron beam.

It should be noted that the distance (pitch) between the dark striation lines varies in some portions of the film. The variation in pitch does not appear to be influenced by induced strains during the cutting process of the films. Pitch has been noted to be affected by inherent viscosity or molecular weight of the polymer (10); specifically, a higher inherent viscosity corresponds to larger pitch or a smaller twist angle. The intrinsic viscosity of CAB used in our investigation is higher than the inherent viscosity of most of the cholesteric copolyesters utilized by Hara et al. (10). This may be the cause for the larger pitch in the structures observed in our study.

Figure 2 (b) shows the TEM of an unstained longitudinal-section of the film containing 20% (w/w) lignin. Banded texture is seen to originate from the surface of the lignin particle which suggests that the occurrence of this particulate phase may serve as a nucleating or terminating surface for the observed ordered structure. (Recall that the lignin and CAB were originally mixed in a solution state and hence phase separation of the lignin domains occurred during solvent evaporation.) We do not have direct evidence for this conjecture since there are other striation lines which do not commence from lignin. This ascertains that lignin is not responsible for the cholesteric morphology but it may enhance its development. This observation is consistant with earlier speculations by Rials and Glasser on the impact of lignin on other solvent cast films of other cellulose derivatives that are known to display liquid crystalline textures (12-13). It should be noted that the spacing between the dark lines is a function of closeness to the lignin particle (see arrows). This suggests that the presence of a surface influences the packing behavior as is often the case in liquid crystalline systems.

The cholesteric structure is not consistently observed in all the regions as these

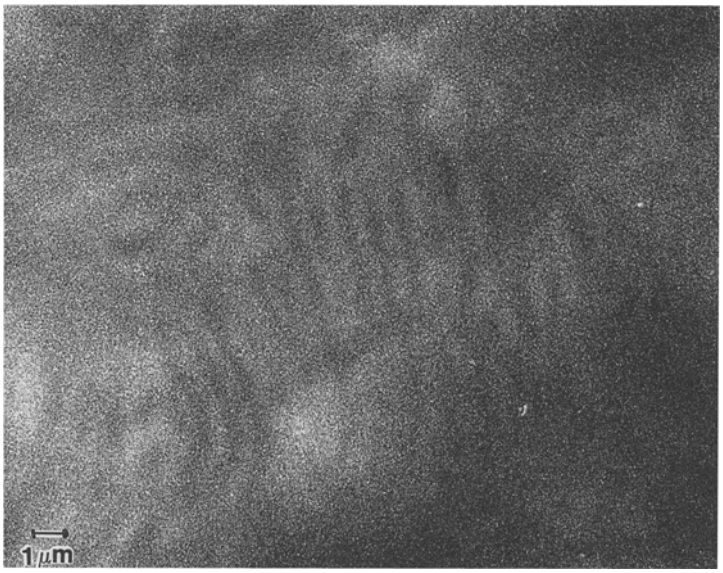

Figure 1. Optical micrograph obtained between cross polarizers of the CAB film containing 20% (w/w) of lignin.

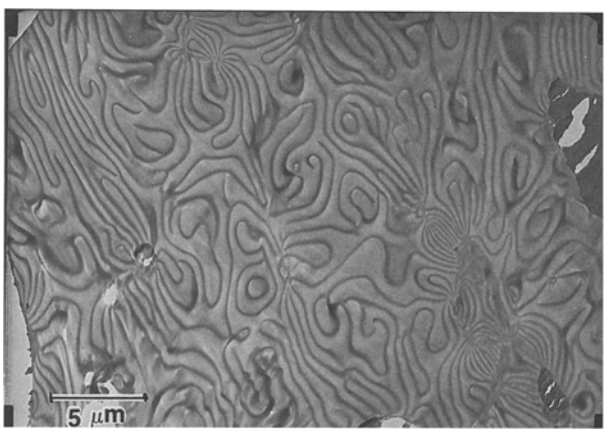

Figure 2A. TEM micrograph of the unstained cross section of a CAB film containing 20% (w/w) of lignin. (View normal to original film plane.)

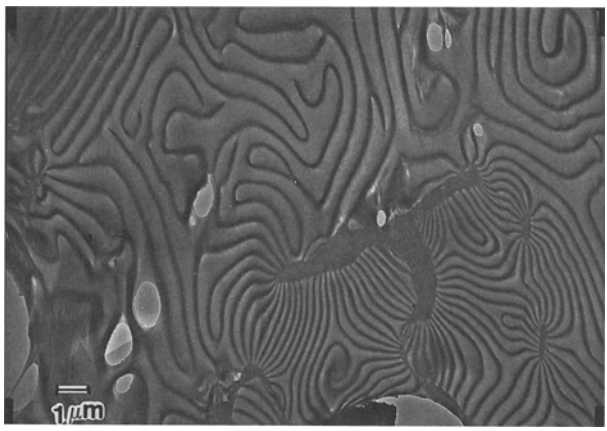

Figure 2B. TEM micrograph of the unstained longitudinal section of the same film shown in Figure 2A but where the view is orthogonal to the film plane.

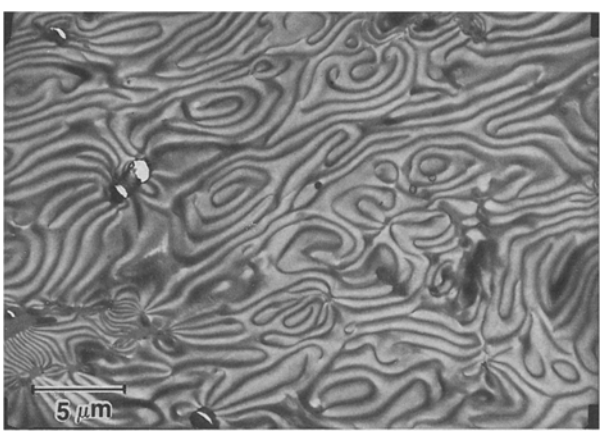

Figure 3. TEM of a CAB film containing 20% (w/w) lignin. The viewer is looking parallel to the normal of the cast stained film.

CAB/lignin films are macrophase separated. This structure, due to possible disruption, is not present in regions where there is a high aggregation of lignin particles. Therefore, this pattern occurs primarily due to the solidified liquid crystalline order from the CAB solution. Figure 3 shows the TEM of the stained cross-section of the film containing 20% (w/w) lignin. While there is some increase in phase contrast due to staining by RuO_4, it is apparent from the previous figure (Fig. 2) that staining is not needed to allow observance of the cholesteric texture. It should be noted that TEM of most of the films had holes.

Future work will concentrate on the processing and morphological characterization of jet/wet spun fibers from these blended liquid crystalline solutions.

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