Band-texture decorated spatial distribution of molecular orientation around air bubbles in hydroxypropyl cellulose aqueous solution

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Summary

The air bubbles in the concentrated hydroxypropyl cellulose (HPC) aqueous solution have been employed to monitor the spatial distribution of molecular orientation around spherical or ellipsoidal particles within the liquid crystalline matrix. The deformation of the air bubbles under shear flow was observed in a polarizing microscope. The stream lines are curved near air bubbles. Corresponding spatial distribution of the molecular orientation was revealed by the technique of band-texture decoration. Associated pleated morphology was also observed in a scanning electron microscope.

Introduction

Liquid crystalline polymers (LCPs) are characterized by rigid or semirigid molecular chains, and hence exhibit distinct physical properties not to be expected in common flexible polymers. The molecules of the LCPs are easily oriented in the direction of shear. Because of the high degree of the molecular orientation, the LCPs have high modulus and strength along the shear direction (1-4). However, the mechanical strength may be reduced by the remained defects, impurities or air bubbles. How these factors influence the molecular orientation and hence mechanical properties of liquid crystalline matrix become, therefore, a topic of interests. For a first step along this line, the present paper studied the supermolecular organization induced by the air bubbles in the concentrated hydroxypropyl cellulose (HPC) aqueous solution.

One of interesting and puzzling phenomena about LCP is the band texture (5-37). Under crossed polars, LCPs exhibit the alternating dark and bright bands with the width of micron meters. Besides of interest in the light of the fundamental research, the band texture affects the mechanical properties of LCP materials very much (32) and, therefore, attracted much attention of scientists and engineers. This paper observed the band texture in LCP around air bubbles. Since the bands are usually perpendicular to the preshearing direction (exactly to say, perpendicular to the orientation of the original local shear stress), they can be employed, as a decorator, to indirectly detect the spatial distribution of the original molecular orientation or of the

original local shear stress during shear flow. Besides the polarizing optical microscopy (POM), scanning electron microscopy (SEM) was applied to observe the bands, by which the pleated morphology was confirmed around air bubbles. The deformation of the air bubbles were also observed in a time-resolved polarizing optical microscope.

Experimental

HPC was supplied by TCI (*MW* 6000). The HPC is a kind of semirigid macromolecules. The lyotropic liquid crystal was prepared by mixing HPC and water at room temperature followed by centrifugation to remove most of air bubbles. The solution (50 wt %) was sheared between two glass slides placed in a simple self-conduct shear apparatus. The shear apparatus is placed in a polarizing microscope and the shearing process can hence be observed in real time. In order to observe band textures clearly, the dry films were also prepared immediately after shearing, by fast drying the wet film with a strong electric cold-wind-blower lasting for 20 sec. The wet and dry films with depth about 40 µm and 20 µm, respectively, were observed in a Leitz polarizing optical microscope. The source is the white light with orthoscopic incidence. The micrographs were captured by a CCD (charge coupled device) with 512×512 pixels and 256 relative intensity levels. The dry film was further observed in a Hitachi S-520 scanning electron microscope (SEM) after spurting Au on the film surface.

Results and discussion

Due to high viscosity of the concentrated HPC aqueous solution, some air bubbles remain after centrifugation (Figure 1). The concentrated solution is in the liquid crystalline state. Since the solution remains some memory of preshearing history, the matrix in Figure 1a is actually regarded as in the nematic state with the molecules orientated parallel to the shearing direction. Considering the observation was made in the orthogonal position (the polarizer is parallel to the shearing direction), the incident light cannot transmit the anisotropic matrix under crossed Nicols, except the region near air bubbles. The pattern of the bright four-lobes around air bubbles (Figure 1a) is similar to that resulting from the interfacial stress around spherical rubber filled in epoxy resin (38). In contrast to this, the depolarization in the present paper comes from the inclined molecular orientations around air bubbles due to the spherical geometry. The deformation of air bubbles is shown in Figure 1b. The elongation of the air bubbles arises from the existence of the normal stress difference. Obviously, the stream lines and the orientation of the principal local shear stress are curved around air bubbles.

The deformation of the air bubbles is fast recovered (Figure 2). It is well known that band textures are formed in main-chain LCPs during shear relaxation if the preshearing rate is above a critical value. No band textures are observed at low preshearing rate (Figure 2), while they can be seen obviously at high preshearing rate (Figure 3). In order to obtain a high contrast ratio (36), the polarizer and analyser have been rotated simultaneously by about 30° (Figure 3a). As usual, the bands are perpendicular to the preshearing direction. It is the case in the regions far away from the air bubble (Figure 3a). However, the bands are curved in the region near the air bubble as seen in Figure 3a and more clearly in Figure 3b around a larger air bubble.
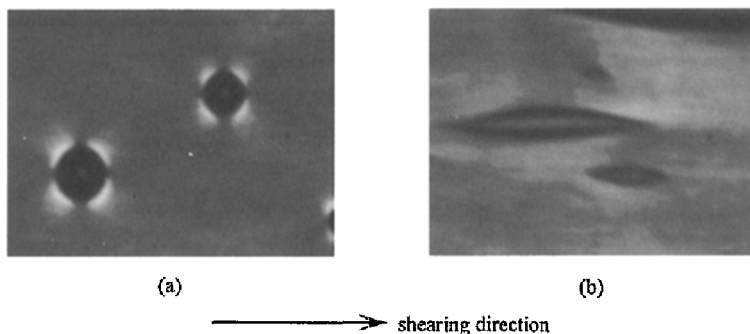
(a)   (b)

⟶ shearing direction

Figure 1. Polarizing micrographs of the film of HPC/H$_2$O solution containing air bubbles. (a) in the quiescent state; (b) in the shear state with the shear rate about 300 s^{-1} (for another view field). The larger bubble in (a) is with the radius about 15 μm.

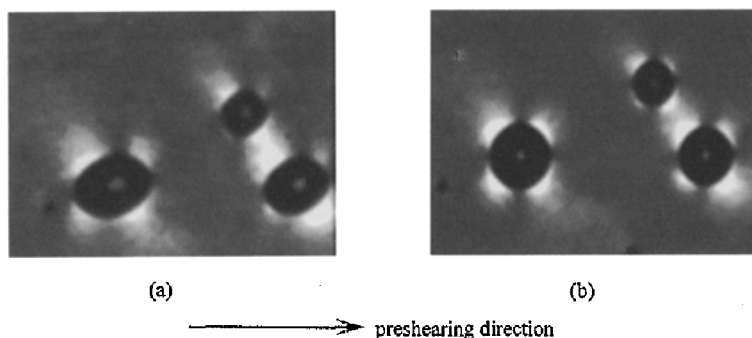(a)   (b)

⟶ preshearing direction

Figure 2. Polarizing micrographs of the film of HPC/H$_2$O solution containing air bubbles. (a) just cessation of shear flow with the shear rate about 50 s^{-1}; (b) after 4 s. The largest bubble in (b) is with the radius about 15 μm.

It is believed that the band textures result during the non-linear relaxation process of LCP on the release of the stored elastic energy due to preshearing, although the detailed mechanism of the formation of bands is far from being resolved. It is well known (5-37,39) that the local bands align in the direction perpendicular to the principal direction of the local stress and hence to the original orientation of rigid or semirigid main-chain macromolecules induced by the preshearing. Therefore, the band textures seen in Figure 3 turn out to be employed as a monitor to detect the spatial distribution of local molecular orientation around a spherical particle immersing in a LCP matrix as presented in Figure 4. In fact, the band-texture decoration has been successfully applied to study the internal stress field among disclinations by Chen et al. (39), following the wonderful technique of the lamellae decoration introduced by Wood et al. (40-44) to observe the orientation of crystalline and liquid crystalline polymer chains.
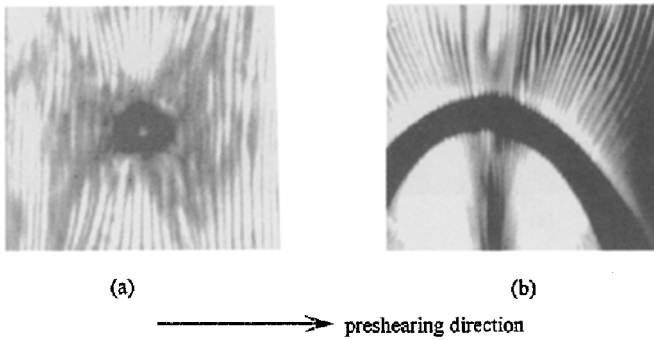
(a)   (b)

———————————▷ preshearing direction

Figure 3. Band textures around two air bubbles in the sheared film of HPC/H$_2$O solution. The preshearing rate is about 1,300 s^{-1}. The band periods in (a) and (b) are about 4 µm.
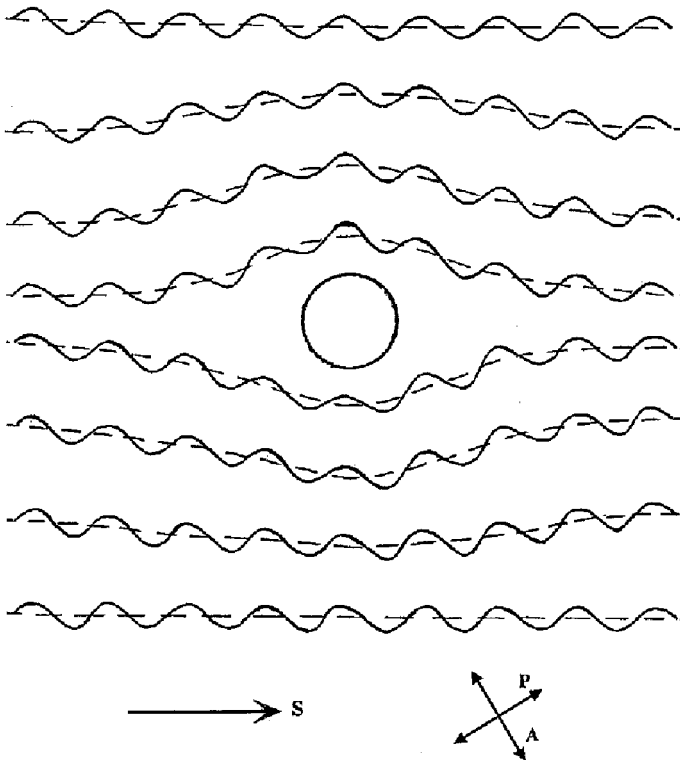

———————————▷ S

Figure 4. Schematic representation of the molecular orientation of HPC around an air bubble. The dashed lines indicate the original molecular orientation around the air bubble due to preshearing along the direction S. The solid lines denotes the sinusoidal molecular orientation formed during the relaxation after cessation of shear flow, which account for the band texture in Figure 3a observed under crossed polarizer (**P**) and analyser (**A**).

Since the bands are observed in a polarizing microscope and the extinction positions may change with the rotation of the specimen or of both polars (26,36,37), the band texture is commonly regarded as a polarizing optical effect arising from the periodicity of molecular orientation along preshearing direction,. The supermolecular structure or the arrangement of the local optic axes associated with these bands is, according to our previous paper, sinusoidal, by comparison between experimental micrographs and theoretical birefringence patterns (36,37).

However, the band texture is not merely a polarizing optical phenomenon. Even in a scanning electron microscope, the periodic bands can be seen (Figure 5). In this case, no cross polars are used at all, and the bands results from the pleats. In SEM observation, the detector is located on the left-hand side above the sample, therefore, the section of the molecules or fibrils facing the detector appear brighter than the section facing away from the detector. The pleats were early observed by Nishio *et al.* (13), and the contractional strain has been considered responsible for the out-of-plane component. We would like to indicate that the pleat period obtained by SEM is consistent with that obtained by POM ($\sim$ 4 μm). This implies that the orientation adjustment and the mass flow immediately after cessation of shear flow are coupled in the formation of the band textures and might be meaningful for revealing the mechanism of band formation.

950580 20KV X1.00K 30um

$\longrightarrow$ preshearing direction

Figure 5. SEM micrograph of the presheared HPC film containing an air bubble.

The detailed effects of air bubbles and band textures to the mechanical properties of the main-chain LCP materials is an open question at the present time. The formation mechanism of the band texture has not been resolved, although some hypotheses have been put forward and seem to be helpful (27,28). Further investigations are, therefore, desired.

Acknowledgments

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