Control of the Anisotropic Mechanical Properties of Liquid Crystal Polymer Films by Variations in Their Banded Texture

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ABSTRACT: Variations in the banded texture of sheared liquid crystal polymer films are shown to control the anisotropy of their mechanical properties. Films, prepared by shearing lyotropic liquid crystal polymer solutions of 2-hydroxypropyl cellulose, were submitted to elongation both along and normal to the shear direction. The films were found to be brittle along the shear direction and ductile in the transverse direction. Stretch along the shear direction does not significantly affect the molecular orientation for any of the films. However, in the transverse direction, profound molecular reorientation occurs on stretching the film, resulting in a fibrillar structure, except at very small band wavelengths. After the disappearance of the original bands due to the deformation in this transverse direction, new bands appear which are of a much smaller wavelength.

Introduction

Liquid crystalline polymers (LCPs) are characterized by rigid or semiflexible 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. After the cessation of this shear stress, both thermotropic and lyotropic LCPs develop a characteristic banded texture not found in common flexible polymers.[1-10] These bands run perpendicular to the direction of shear, and represent a periodic fluctuation of the molecular orientation around the shear direction. An alternating tilt angle of the optic axis of the macromolecule of equal and opposite values, relative to the shearing direction, is considered to be the reason for band formation.[5,11-13] This periodic oscillation of the orientation of the director has been related to the elastic behavior of liquid crystal systems and attributed to contraction strains of the sheared sample induced by stress relaxation after cessation of flow.[6] The factors affecting the formation of such a texture, however, are still being investigated in detail.

Because of the high degree of molecular orientation, the LCPs exhibit high modulus and strength along the shear direction.[14-21] However, the mechanical strength in the transverse direction is relatively low. These anisotropic mechanical properties are consistent with the molecular orientation which results from the flow of the mesomorphic state under shear stress.[18-21] Hikmet and Broer[21] observed brittle behavior in the direction parallel to the molecular orientation and ductile behavior in the direction perpendicular to the molecular orientation of thin films formed from polymerizing oriented liquid crystalline acrylates. White[19] attempted to produce biaxially oriented films with equal properties in all directions in the plane from para-linked aromatic polyamides.

There have been many reports regarding anisotropic mechanical properties of oriented polymers.[22-27] Seferis and Mccullough[22,23] related the directional dependence of the mechanical properties of anisotropic, partially crystalline polymers to the percent crystallinity and characteristics of the crystalline and amorphous components. They also set up models to predict the dependence of the longitudinal and transverse moduli of anisotropic polyethylene on percent crystallinity and the state of molecular orientation. Ward and Hadley[24] also have discussed the anisotropic behavior in terms of two structural models: an aggregate model in which the polymer is considered to consist of aggregates of highly anisotropic units, and a

Table I
Relationship of Mechanical Properties to Wavelength of Banded Textures in HPC 20-μm Films

band length, μm	direction[a]	strain at break, %	stress at break, kg mm^{-2}	modulus, kg mm^{-2}
2.95	along	45.22	0.51	16.43
2.95	transverse	16.60	0.16	14.48
8.20	along	25.95	1.12	19.92
8.20	transverse	89.33	0.13	8.68
9.00	along	46.48	0.78	25.19
9.00	transverse	200.10	0.10	7.19
12.50	along	32.80	0.65	17.36
12.50	transverse	300.00	0.08	4.80

[a] Indicates direction of measurement with respect to the direction of shear.

composite model similar to those used to treat short fiber reinforced composites.

One interesting possibility that has not been discussed or evaluated is that the banded texture, in its detailed control of the orientation of the director, can also be correlated with the anisotropy of the mechanical properties. Hence, one might anticipate that the degree of anisotropy can be related to the wavelength of these bands. In this work, the anisotropy of the mechanical properties of films prepared by shearing the lyotropic liquid crystal polymer solutions of 2-hydroxypropyl cellulose (HPC) are shown to be controlled by the band wavelengths.

Experimental Section

The HPC used was KLUCEL L (95 000 molecular weight) kindly furnished by Hercules Inc. The 37 wt % solutions of HPC in glacial acetic acid were cast using a film casting knife supplied by Gardner Laboratory. Dried films (20 μm) were prepared, and their thickness was measured using a digital micrometer (Mitutoyo). The castings were made on a rigid flat glass plate coated with a fluorocarbon polymer. Films were cast and sheared simultaneously by moving the casting knife at a controlled shear rate of 2000 s^{-1} at four different temperatures: 0, 25, 45, and 85 °C. The films were then dried at these temperatures overnight, followed by further storage at room temperature for another 72 h to yield dried films with different band sizes. The reason for these differences in band size will be discussed later.

After casting and drying, the polymeric films were cut using a stainless steel scalpel into 13-mm by 3-mm test strips in both the parallel and transverse directions with respect to the shear stress. The band wavelength was determined for each sample by observing it under crossed polars on a Nikon microscope.
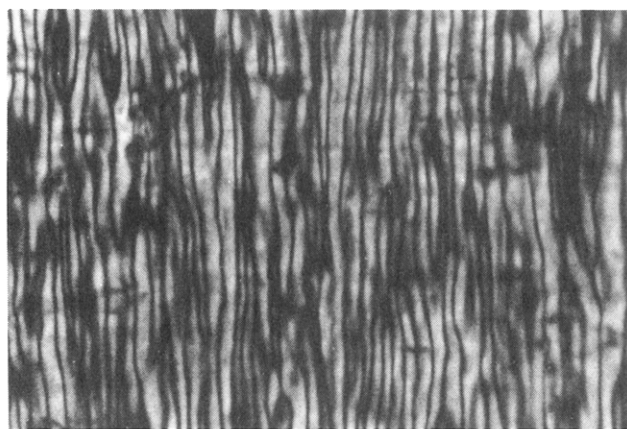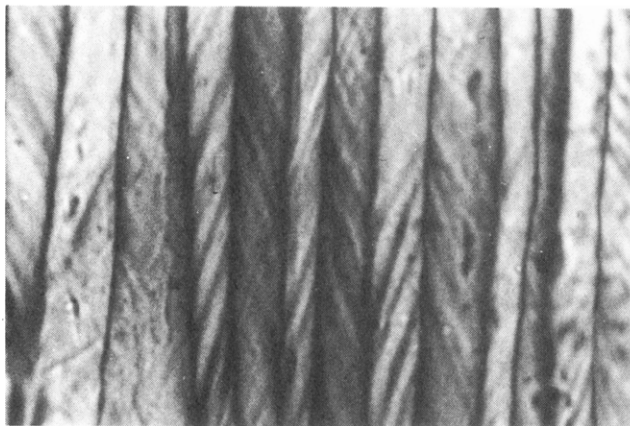
Figure 1. Texture of sheared samples of 37 wt % HPC in AA at different evaporation temperatures: (top) 0 °C; (bottom) 85 °C.

Figure 2. Effect of elongation along the shear direction: (top) 12.5-μm bands; (bottom) 2.95-μm bands.

Photomicrographs were taken using a Nikon Microflex Model EFM semiautomatic attachment.

At each drying temperature, 40 samples were prepared, with half of them having their long direction parallel to the shear mode, and the other half having their long direction along the transverse direction. Tensile tests were performed on an Instron 1122 at a crosshead speed of 10 mm min^{-1} at room temperature. The tensile strength and modulus vs the band size in the two directions is given in Table I. The band sizes are the average value for the sets of 20 samples.

Results and Discussion

When a thin film of 37% HPC solution in acetic acid is sheared by casting, the banded texture appears almost instantaneously after the cessation of shear. The bands then gradually grow larger as the solvent evaporates until they are frozen in. When the solvent evaporation rate is controlled by heating and cooling of the films, different band sizes can be obtained. If the solvent were not permitted to evaporate, the band wavelength would also change with time. The director field is relaxing at some rate that is a function of concentration and temperature, and therefore of the viscoelastic constants of the solution. Putnam and Viney[28] have determined the time dependence of the average band spacing in HPC–water solutions, and found that the bands initially decrease in size as a function of time to a minimum value and then increase with time. If we can take advantage of controlled solvent evaporation at various times, we can obtain films of variable band wavelength. The band size can also be controlled to some extent by controlling the shear rate, but it was found to be more convenient to use a fixed shear rate of 2000 s^{-1},
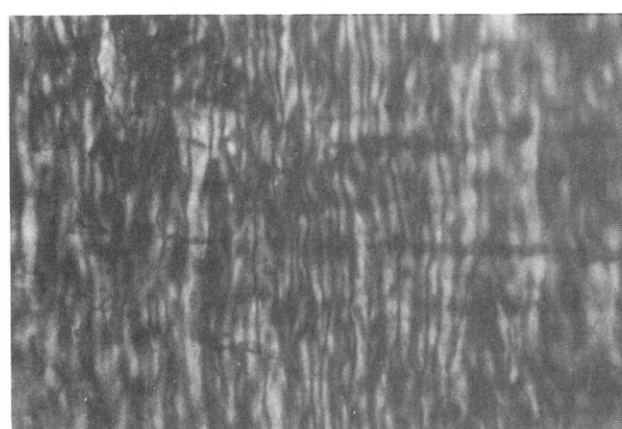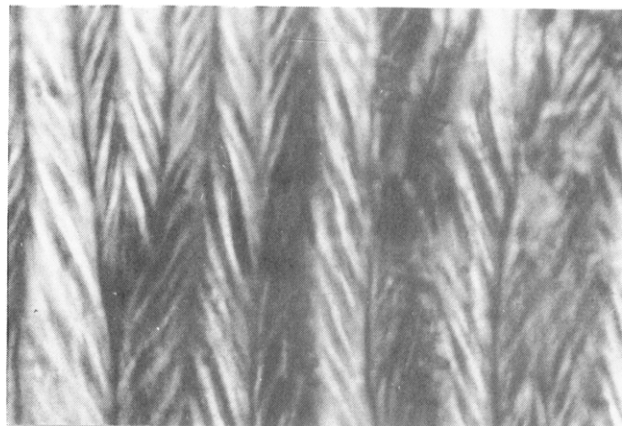
and allow solvent evaporation to produce samples of varying band widths. Figure 1 shows that band size decreases as the temperature of evaporation increases.

It is also possible to determine the amplitude of the director oscillation within the bands. When the polarizer and analyzer are crossed, and the direction of shear is parallel to the polarizer, bright bands and dark lines are alternate and perpendicular to the direction of shear. When the microscope stage is then rotated in a clockwise direction, the image changes as a function of angle, allowing one to measure the tilt angle that the director (or more precisely, the optic axis) makes with the bands. For example, in the film with a band size of 2.5 μm, one bright band becomes totally dark at an angle of 33° which is indeed the tilt angle of the optic axis of the macromolecule relative to the shearing direction. When a 530-nm retardation plate is inserted diagonally between crossed polars and the short side of this plate is the slow vibration direction, yellow bands and blue bands are separated by red lines. As the angle increases, the blue bands gradually become red at 33°. We also measured the tilt angle for films with an 8-μm band wavelength, yielding an angle of 25°. Thus, as expected, the director oscillation decreases with increasing band wavelength.

Figures 2 and 3 show the effect of elongation along the shear direction and normal to the shear direction for different band sizes. It is clear that stretch along the shear direction does not affect the molecular orientation for any of the films, independent of band wavelength. However, in the direction normal to the shear direction, profound molecular reorientation occurs on stretching the film. Figure 3 clearly shows the fibrillar structure which results
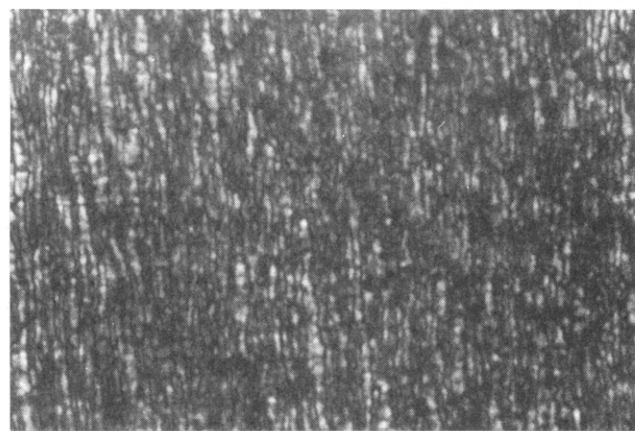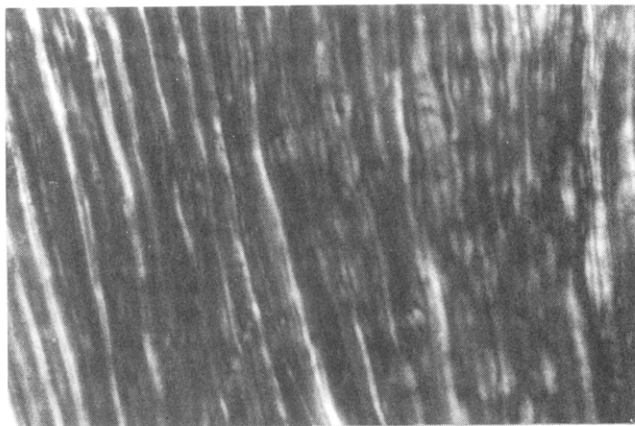
Figure 3. Effect of elongation normal to the shear direction: (top) 12.5-μm bands; (bottom) 2.95-μm bands.
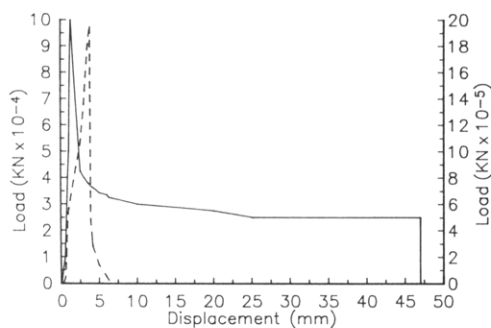

Figure 4. Displacement vs load for HPC films. The dashed line shows the behavior along the shear direction using the vertical scale on the left side of the figure. The solid line shows the behavior in the transverse direction using the vertical scale on the right side of the figure.

from this molecular reorientation. It is important to note that at small bandwidths the effect is much less pronounced. (Figure 3, bottom). After the disappearance of the original bands due to the deformation in this transverse direction, new bands appear which are of a much smaller wavelength as compared to the bands before stretch.

The load-displacement behavior for a sample of 12.5-μm band size is shown in Figure 4. The film is brittle along the shear direction and ductile in the transverse direction. In the transverse direction, the stress reaches a maximum value and then decreases significantly to a value which then remains constant until failure. The deformation occurs nonuniformly, and the sample necks. From a careful observation of optical micrographs at various stages of the elongation process, it appears that molecular reorientation starts to occur when the stress
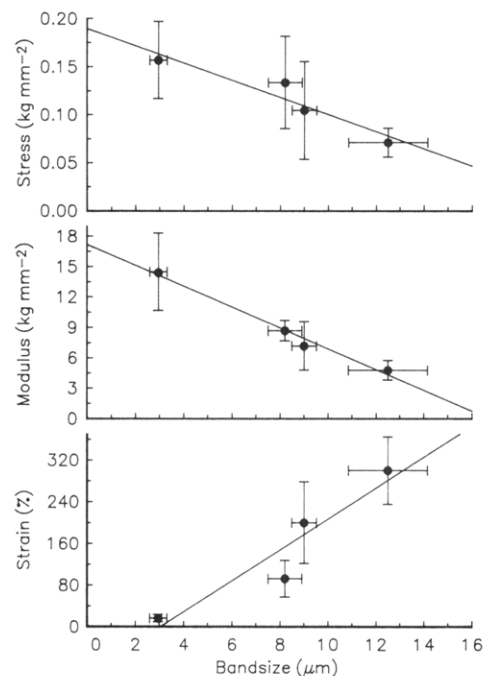

Figure 5. Stress–wavelength, modulus–wavelength, and strain–wavelength relationships for HPC films measured in the transverse direction with respect to shear.

reaches its maximum value, followed by continual cold flow of the sample as the elongation continues. At the zone between the elongated neck and head of the sample, bands are observed parallel to the stretch direction which gradually decrease in size until the middle portion of the elongated neck where the molecules are extremely well aligned and the original bands can no longer be seen. Instead, one observes the fibrillar structure shown in Figure 3.

To demonstrate the complete alignment in this zone of the sample, we focused on an area which showed complete extinction of transmitted light through crossed polarizers. By bringing the optic axis of the molecules into a position parallel to the analyzer, and inserting a 530-nm retardation plate, the dark area becomes red. As the stage is rotated clockwise, the red color gradually turns to blue and then changes back to red when the angle reaches 90°. If the stage is rotated counterclockwise, the red color turns to yellow and then back to red at 90°. Such behavior is typical of a well-oriented uniaxial crystal. In the shear direction, the small increase in bandwidth is simply proportional to the (small) elongation.

The stress–wavelength, modulus–wavelength, and strain–wavelength relationships are shown in Figure 5 for samples stretched in the transverse direction and in Figure 6 for samples stretched along the shear direction. In the transverse direction, as the band wavelength increases, both stress and modulus decrease while the strain increases. Along the shear direction, however, as the band wavelength increases, stress and modulus tend to increase slightly while the strain decreases slightly. Because of the inherently large errors in mechanical test data, the values measured along the shear direction can be viewed as independent of band size within experimental error.

Table I shows that, for each band size, with the exception of the very small band size of 2.95 μm, the stress at break and modulus are smaller and the strain is larger in the transverse direction than in the shear direction. For the 2.95-μm-band films the behavior of the strain is just the opposite. The difference in behavior between the two directions in the film increases as the band size increases:
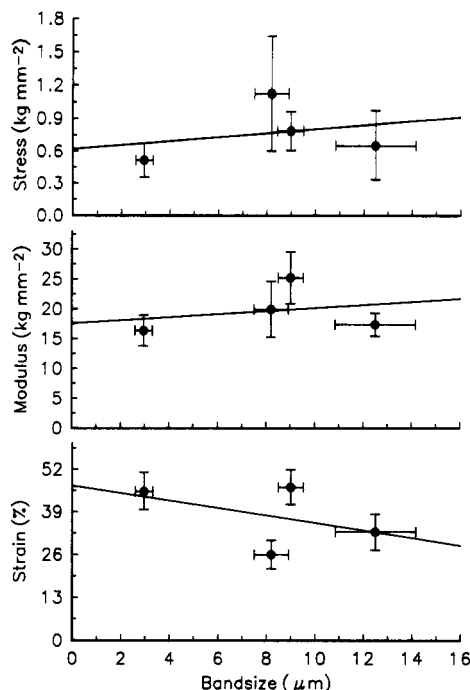
Figure 6. Stress–wavelength, modulus–wavelength, and strain–wavelength relationships for HPC films measured along the shear direction.

in the transverse direction, the strain is 9.1 times larger than that along the shear direction for 12.5-μm bands, 4.3 times larger for 9.0 μm bands, and 3.4 times larger for 8.2-μm bands.

Conclusions

It is evident from the above results that the anisotropic mechanical properties of LCPs are related to the wavelength of the banded texture, and can be controlled by an order of magnitude by adjusting the shear distortion appropriately. Although only lyotropic HPC solutions were used in this work, the phenomenon of banded textures is observed in a wide variety of lyotropic and thermotropic LCPs, and the same type of control of mechanical properties is to be anticipated. Along the shear direction

one expects high strength and low elongation, with essentially no material flow occurring. However, in the transverse direction, stress leads to cold flow and enormous elongation of the sample.

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