Optical Microscopy Study on Poly(*p*-phenylene terephthalamide) Fibers

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Received 28 August 2001; accepted 8 January 2003

ABSTRACT: Two highly oriented poly(*p*-phenylene terephthalamide) (PPT) fibers of different grades, commercially known as Kevlar and Twaron, were examined at high magnification under a transmission optical polarizing microscope in the extinction position between crossed polars. An image with regions of regular fine bands is produced for both classes of fibers, which is interpreted to be due to the passage of depolarized scattered light from a material with regularly spaced discontinuities. These bands reflect the periodic pleat structure of the fibers. The fibers were chemically etched, coated with gold, and investigated under a Nomarski differential interference contrast microscope in the extinction position between crossed polars. The observation for Kevlar fibers shows a clear periodicity of transverse bands perpendicular to the fiber axis, but this is much less evident for Twaron fibers. The etchant gives smooth, nearly flat sections through the Kevlar fibers, whereas it is not very effective for the Twaron fibers. The variable wavelength interferometry (VAWI) technique, which is valuable for studying highly oriented polymeric fibers, is used to measure the mean refractive indices and birefringence of a fiber as a function of light wavelength. The results show that these fibers absorb the surrounding liquid, which may change their optical properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 360–369, 2003

Key words: polyamides; fibers; optics; refractive index; structure-property relations

INTRODUCTION

Poly(*p*-phenylene terephthalamide) PPT fibers represent a class of materials that are of great interest because of their exceptional mechanical properties.[1] These fibers belong to a group of highly oriented fibers. They are also termed high-performance synthetic organic fibers. These fibers possess a high tensile modulus (in the range 70–150 GPa). Kevlar and Twaron are trade mark names of PPT fibers. Kevlar 49 fibers, for example, have outstanding physical properties and are used as reinforcement for composite materials. Dobb et al.[2,3] studied the supermolecular organization of Kevlar 49 fibers using a combination of electron diffraction and electron microscopic dark field imaging techniques. They concluded, from observations on longitudinal sections, that the supermolecular architecture of these fibers consists of a system of radially arranged sheets regularly pleated along their long axes. Hagege et al.[4] showed a radial morphology in Kevlar fibers by optical microscopy; their electron microscopic results indicated some finer structural organization within the radial zone.

Avakian et al.[5] claimed observation of a 200–300 nm periodic spacing along the fiber axis in HCl-etched and fractured fibers, but did not indicate whether this structure was located in the core or the skin regions. They concluded that the periodic spacing was consistent with the pleated sheet morphology originally suggested by Dobb et al.[2,3] Morgan et al.[6] have also reported seeing a periodic banding along the fiber axis in SEM micrographs of fractured Kevlar 49 fibers. No work has been published on this specific method of research within the last ten years.

The spectral dispersion of the refractive index is a measure of the degree of variation of the refractive index with wavelength. Total dispersion is the term applied to the numerical difference between the refractive indices of the material for wavelengths at opposite ends of the visible spectrum. Interference systems suffer from the spectral dispersion of the refractive index, or birefringence which usually causes the zero-order fringe to be colored in white light when the differences in the mentioned dispersion among the object, its surrounding medium and the interference system are not balanced. Thus, the crucial problem of any measuring technique involving interferometry is the determination of the interference order in the image of the object under study. Variable wavelength interferometry (VAWI), devised by Pluta,[7–11] is one of the most successful approaches. This technique is especially suitable when used jointly with Pluta's double-refracting interference microscope[12] fitted with a halogen lamp and a wedge interference filter. Pluta[8] has processed this technique with a computer con-

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Journal of Applied Polymer Science, Vol. 90, 360–369 (2003)

TABLE I
Physical Properties of Samples Used

	Linear Density (N/Tex)	Breaking Extension (%)	Breaking Strength (N/Tex)	Initial Modulus (N/Tex)	Initial Modulus (GPa)
Kevlar 13	0.162	1.85	1.80	52.33	77.52
Kevlar 17	0.150	2.73	2.63	68.09	74.63
Twaron 001	0.269	2.57	2.46	87.30	99.90
Twaron 601	0.140	2.11	2.15	81.86	116.33
Twaron 602	0.140	1.92	1.80	72.79	101.62

trolled automatic analysis system,[9] which allows one to measure the spectral dispersion curves and the refractive index profile of a cylindrical fiber automatically.

This study reports some aspects of the structure of two samples of Kevlar and Twaron fibers by applying three microscopes. The first microscope is the optical transmission polarizing microscope, which was described first by Simmens and Hearle.[13] The second microscope is the Nomarski differential interference contrast microscope. The third microscope is the two-beam polarizing interference microscope devised by Pluta.[12]

EXPERIMENTAL

Materials

Two sets of experimental commercial samples of the Kevlar and Twaron types were used in this study. Kevlar (produced by EI DuPont de Nemours, Wilmington, USA) and Twaron (produced by Akzo Nobel, Arnhem, the Netherlands) are manufactured by different processes whose details are private to the companies. These fibers have the mechanical properties listed in Table I, as they have been reported.[14]

Microscopy

The PPT fibers were stretched over a low-density rubbery ethylene-propylene copolymer, and were then buried in a thin layer of molten trans-polyisoprene at approximately 60°C, which solidified on cooling. They were then etched for approximately 1 h, chosen to be sufficient to remove the covering polyisoprene and reveal central section through the fiber. The etchant was a 1% solution of potassium permanganate in a mixture of 4 volumes orthophosphoric acid (85%) and 1 volume water, similar to that used for the permanganic etching of PEEK polymer.[15,16] The etched fibers were coated with gold and then investigated under a Nomarski differential interference contrast microscope in the extinction position between crossed polars.

All five PPT fibers were investigated using the VAWI technique. The fiber was mounted on a glass slide, a drop of suitable immersion liquid was put on the sample if necessary, and then it was covered by a cover slip. The field of view was adjusted, and the diameter of the fiber was measured using the software attached to the computer linked to the Pluta microscope. The value for the refractive index of the immersion liquid in addition to the fiber diameter were inputted and the software was allowed to run. By the end of the run, the computer provided the spectral dispersion curve of the fiber, and a recorded micro-interferogram at random wavelength.

Theoretical considerations

The VAWI technique[10,17] depends on selecting particular wavelengths $\lambda_s = \lambda_1 > \lambda_2 > \lambda_3 > \ldots$, which are achieved by adjusting the wedge interference filter, for which interference fringes displaced by the fiber under study become consecutively coincident and anti-coincident side by side with the reference empty fringes. Thus, the interference order increments $q_s = 0, 0.5, 1, \ldots$ is observed. The corresponding interference spacing $b_s = b_1, b_2, b_3, \ldots$ are measured with the help of the micrometer screw linked to the microscope. The equivalent wavelength values $\lambda_s = \lambda_1, \lambda_2, \lambda_3$ are read out from the calibration graph $b(\lambda)$ of the optical system of the instrument.[10] The optical path differences, $\delta_s = \delta_1, \delta_2, \delta_3$, are determined from the right-hand side of the following equation

$$\delta_s = (n_s - n_L)t = (m_1 + q_s)\lambda_s = m_s\lambda_s \qquad (1)$$

Where n_s is the refractive index of the fiber, which is characterized by the dispersion curves $n_s(\lambda)$, and $n_L(\lambda)$ for the surrounding medium; m_1 is an integer number, called the initial interference order, which occurs at the starting coincidence of longer wavelengths, $\lambda_s = \lambda_1$, and q_s is the increment (or decrement) of the current interference order m_s with respect to m_1 when the wavelength of light is changed from λ_1 to λ_s.

The initial interference order m_1 can be calculated from two approximated formulae[10,11]:

$$m_1 = q_s[\lambda_s/(\lambda_1 - \lambda_s)] \qquad (2)$$

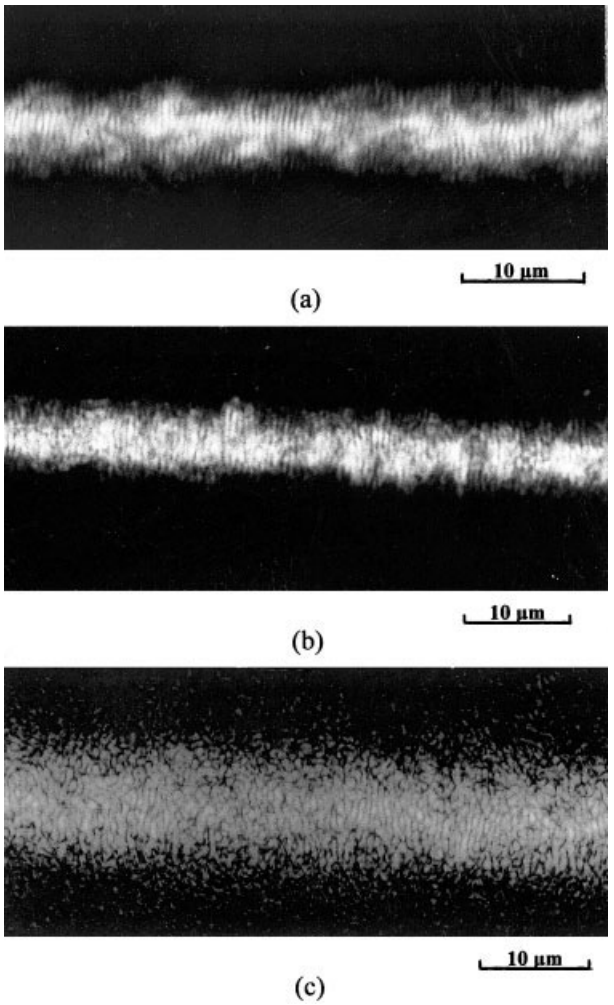


Figure 1 Transmission optical micrograph of Kevlar 13 fiber viewed between crossed polarizers at the orthogonal position using monochromatic light of wavelength: (a) 546 nm, (b) 590 nm, (c) 632.8 nm using He-Ne laser.

and

$$m_1 = q_s[b_s/(b_1 - b_s)] \tag{3}$$

Pluta[18] gave the circumstances of these approximations and the method to check that m_1 has been correctly accepted. Optical path differences, δ_s, are calculated from eq. (1), and the refractive indices are determined from the following equation:

$$\delta = z_o\lambda/b = (n - 1)t \tag{4}$$

where t is the fiber thickness, and the fiber is surrounded by air instead of a liquid. Pluta[8,9] has developed this technique with a computer-controlled automatic analysis system instead of using manual measurements. The refractive index profile of a fiber measured by this technique is counted according to the theory developed by Sochacki.[19]

RESULTS AND DISCUSSION

The optical microscope has played an important role in the analysis and study of fiber structure. Most fibers are anisotropic materials because of fiber spinning and drawing. The growth mechanism in fibers, which produces birefringence and oriented systems, can be studied by a polarized light microscope. Optical microscopy has the ability to use the phenomenon of polarization in imaging; this has many applications to polymers. When the fiber is viewed between crossed polars, the image contrast achieved derives from variations in the thickness of the fiber from one location to another. PPT fibers were mounted in an immersion liquid with refractive indices 1.5708, 1.5652, and 1.5644, corresponding to wavelengths of 546, 590 and 632.8 nm, respectively, at a temperature of 30°C. The

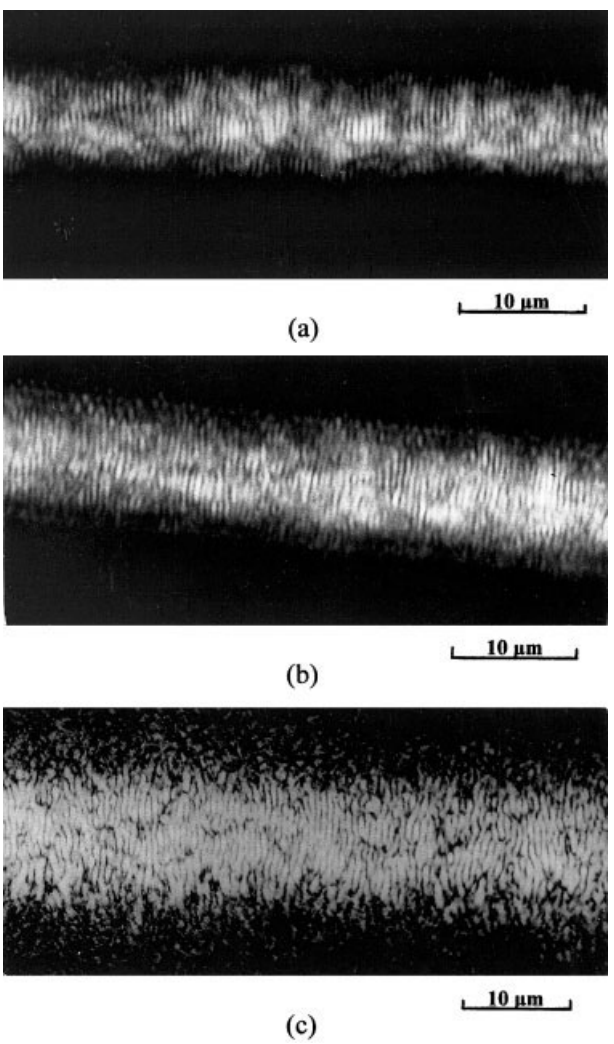


Figure 2 Transmission optical micrographs of Kevlar 17 fiber viewed between crossed polarizers at the orthogonal position using monochromatic light of wavelength: (a) 546 nm and (c) 632.8 nm In (b), the fiber axis is at 5° to the polarizer axis using monochromatic light of wavelength 546 nm.

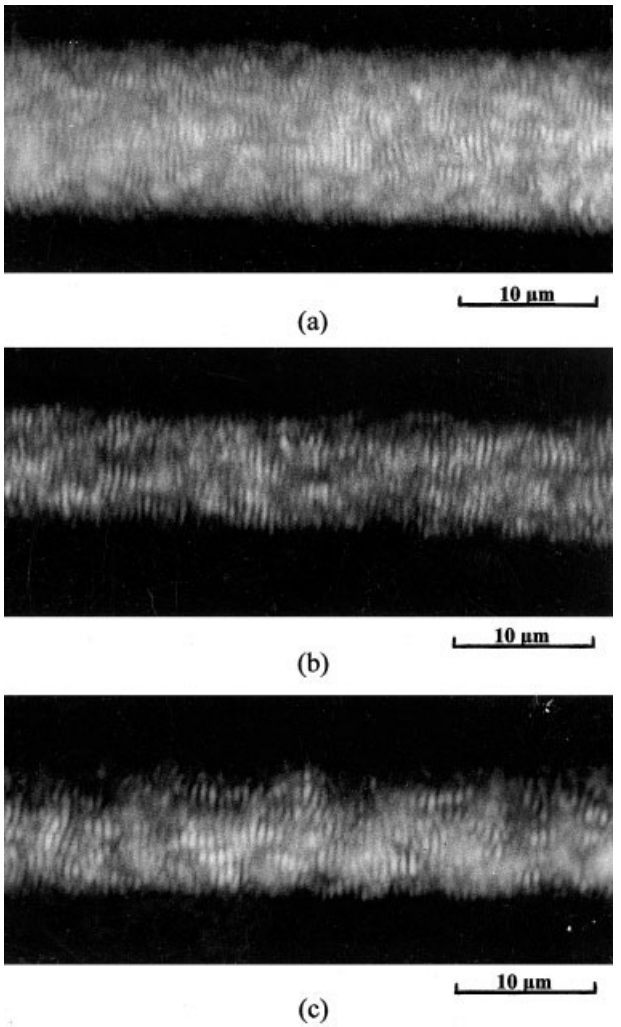


Figure 3 Transmission optical micrographs of fiber viewed between crossed polarizers at the orthogonal position using monochromatic light of wavelength 546 nm for (a) Twaron 001, (b) Twaron 601, and (c) Twaron 602.

fibers were placed in the transmission optical polarizing microscope at the orthogonal position, the position parallel to the plane of either the polarizer or the analyzer and were illuminated by monochromatic light. The appearance of Kevlar fibers under these conditions is illustrated in Figures 1 and 2. The appearance of the fringes did not change with the type of light source, but when differently coloured interference filters were used, it was observed that fringe spacing changed. Under green light [Fig. 1(a)] they are more closely spaced than under yellow [Fig. 1(b)], and their spacing is coarsest under red light [Fig. 1(c)]. This change in spacing with the wavelength of light may lead to the conclusion that the bands observed when imaging the fiber in the extinction position must be interference fringes and not true images. The fringes appeared even when the fiber axis was oriented at 5° to the polarizer, as shown in Figure 2(b). However, in the diagonal position, these fringes were not visible. The same observations are obtained for the Twaron fibers of different grades shown in Figure (3). Thus, we agree with Simmens and Hearle,[13] that the bare interpretation of the optical evidence is that the appearance of bands under these conditions can be explained as the result of a periodic occurrence of light scattering regions in the fiber. There could be a number of structural reasons for this.

A particular application of polarization microscopy, which has considerable value in studying the surfaces of polymers, is the use of the Nomarski differential interference contrast microscope. The appearance of etched Kevlar fibers under this microscope is illustrated in Figures (4) and (5). The etchant simultaneously removes the embedding polymer and ablates the fiber, thereby avoiding mechanical damage due to microtome cutting. It gives smooth, nearly flat sections through the fibers. It reveals a pleat structure similar to that revealed by ion etching,[20] but with gentle variations in relief which are much more suitable for re-

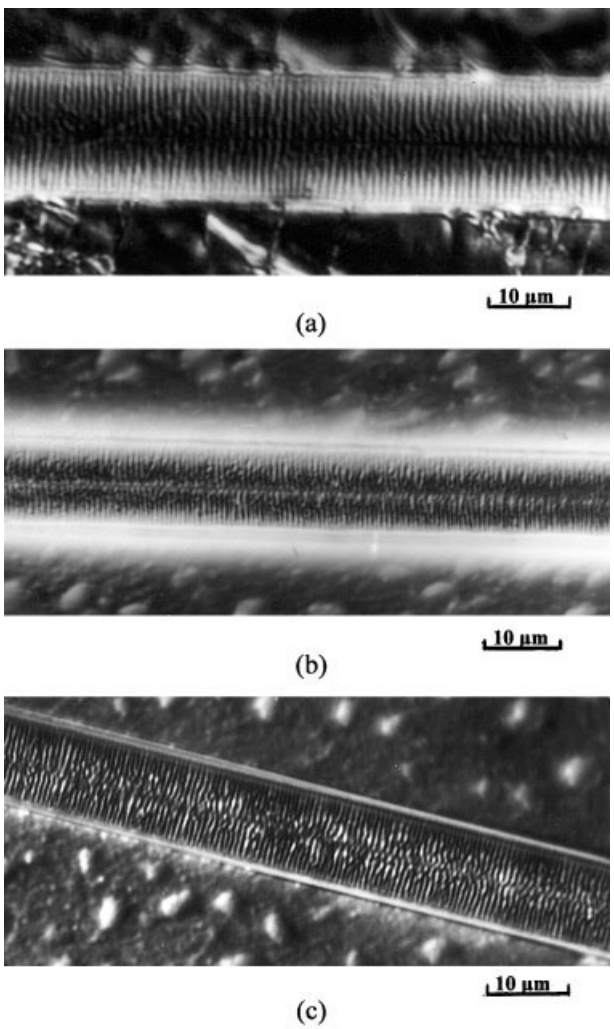


Figure 4 Nomarski differential interference contrast micrograph of etched Kevlar 13 fiber at the (a,b) orthogonal position, and the (c) diagonal position, applying white light.

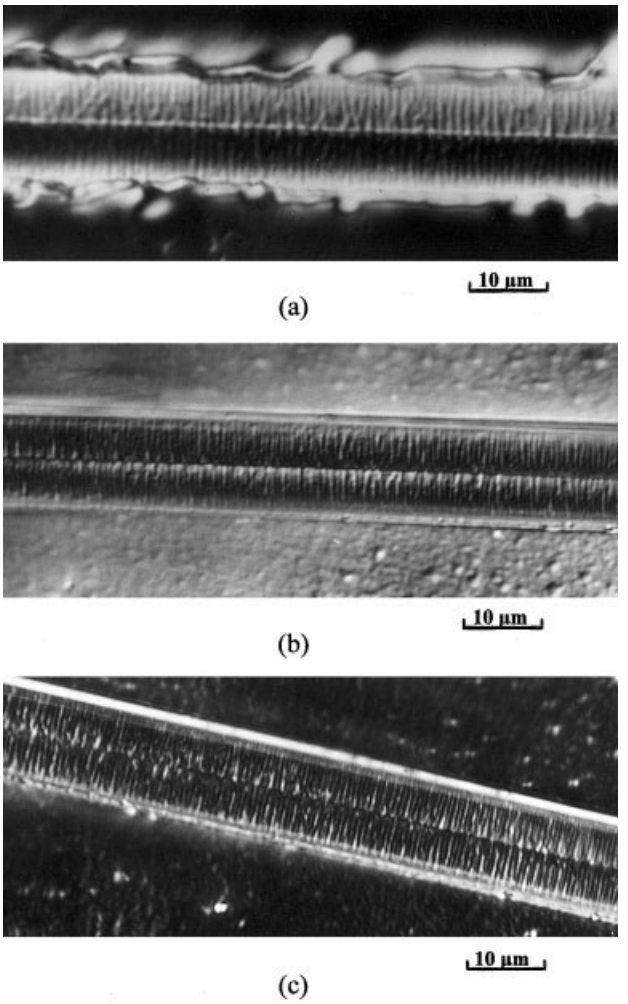


Figure 5 Nomarski differential interference contrast micrograph of etched Kevlar 17 fiber at the (a,b) orthogonal position, and the (c) diagonal position applying white light.

vealing under Nomarski reflection than the deeply grooved surfaces produced by other techniques. The variation of the contrast in these results is due to the periodicity pleat structure of Kevlar fibers, which appears when the fiber axis is oriented at any angle to the polarizer. The etchant left some fibers rounded, as in Figures 4(a) and 5(a), and other fibers flat, as in Figure 4(c). There was, however, an overall tendency to give prismatic sections to fibers, rather than flat or, where the fiber is exposed, rounded sections. The cause is most likely to be differences in vorticity arising as the etchant flows first one way, then the other in the reciprocating shaker. This has the effect of giving a slight tilt between the two halves of otherwise flat etched surfaces of fibers as in Figure 5 (b,c): the central line down these sections may, therefore, be an artifact but it could also contain an actual central singularity in the pleat structure. Twaron is produced by a different process than Kevlar, and has a different internal structure. Twaron 001 in Figure 6(a) shows a longitudinal 'fibrillar' structure, periodically interrupted by transverse breaks that may be the same in character as the pleats in Kevlar. This longitudinal structure appears also, but in a more irregular manner, in Twaron 602 in Figure 6(c). Twaron 601 fiber appears to be more similar to Kevlar, as shown in Figure 6(b). The uppermost fiber in Figure 6(a) shows an elliptical section, where it is emerging from being buried under the polyisoprene, while the lower fiber is etched down to a nearly diametral section. This lower fiber shows some diagonal kink bands that are characteristic of Twaron fibers but are also sometimes seen in Kevlar. These arise because aramid fibers are weak under compression,[21,22] and they can even be formed by stresses arising during molding of composites.[23] This etching technique has also been used to study the finer structure of Kevlar fibers under the scanning electron

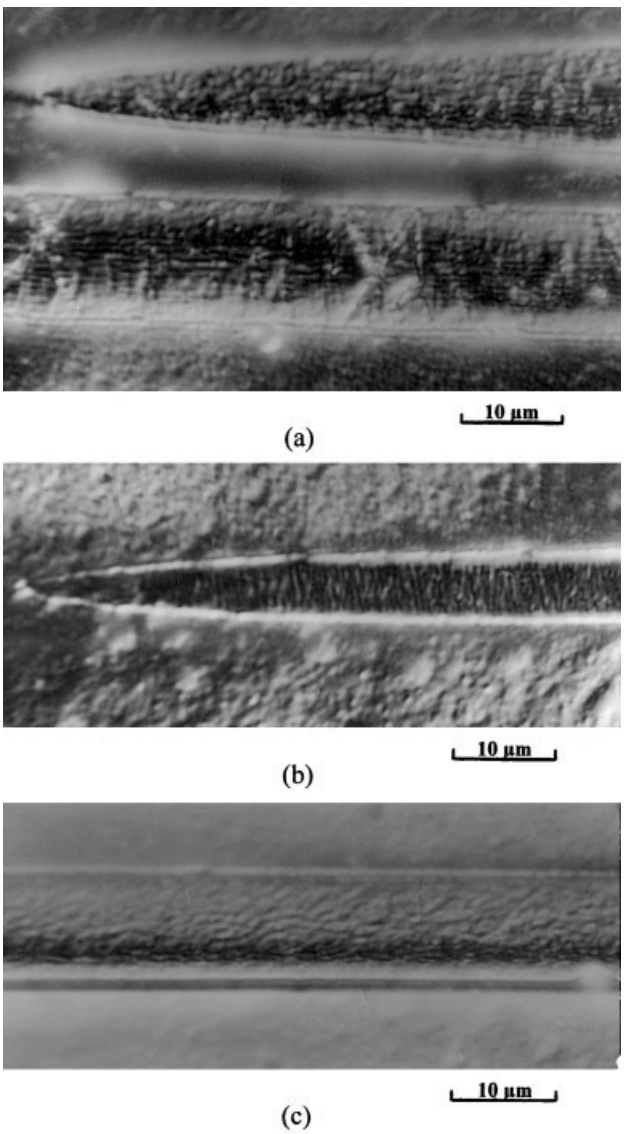


Figure 6 Nomarski differential interference contrast micrograph at the orthogonal position for etched (a) Twaron 001, (b) Twaron 601. and (c) Twaron 602 fibers, applying white light.

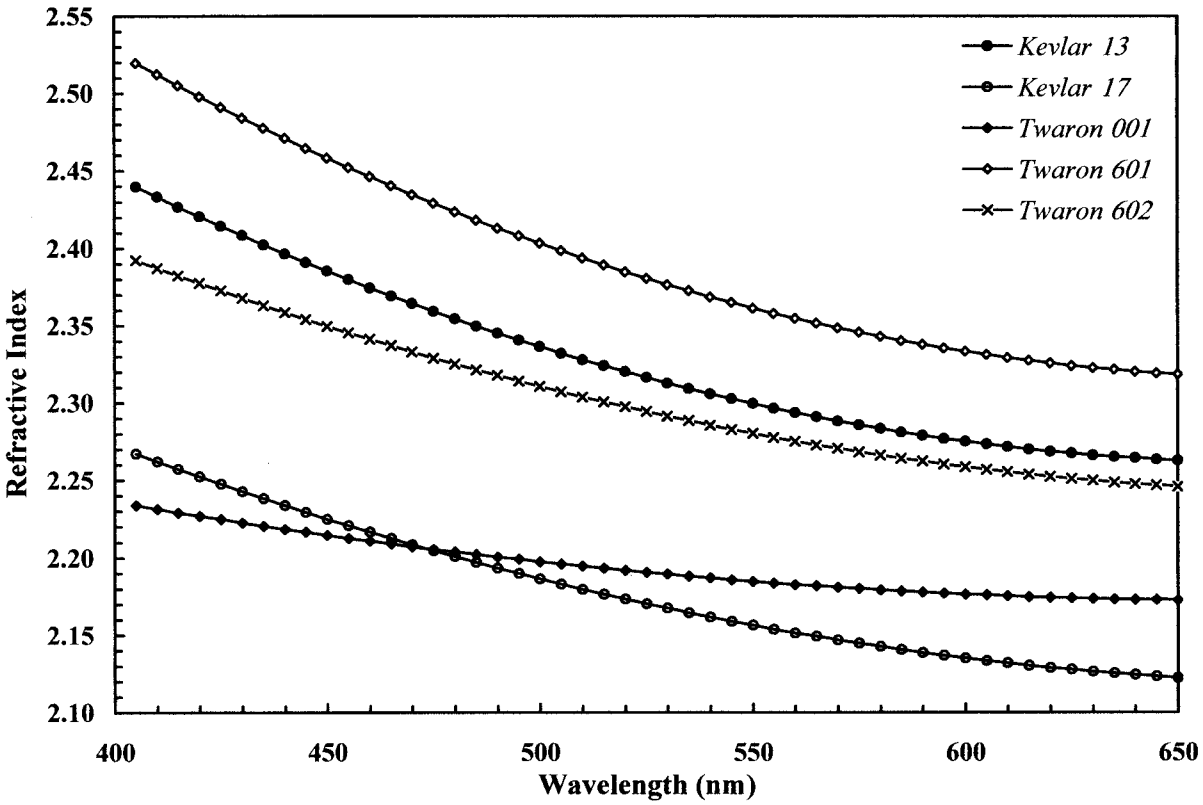


Figure 7 The spectral dispersion curves of PPT fibers for light vibrating parallel to the fiber axis.

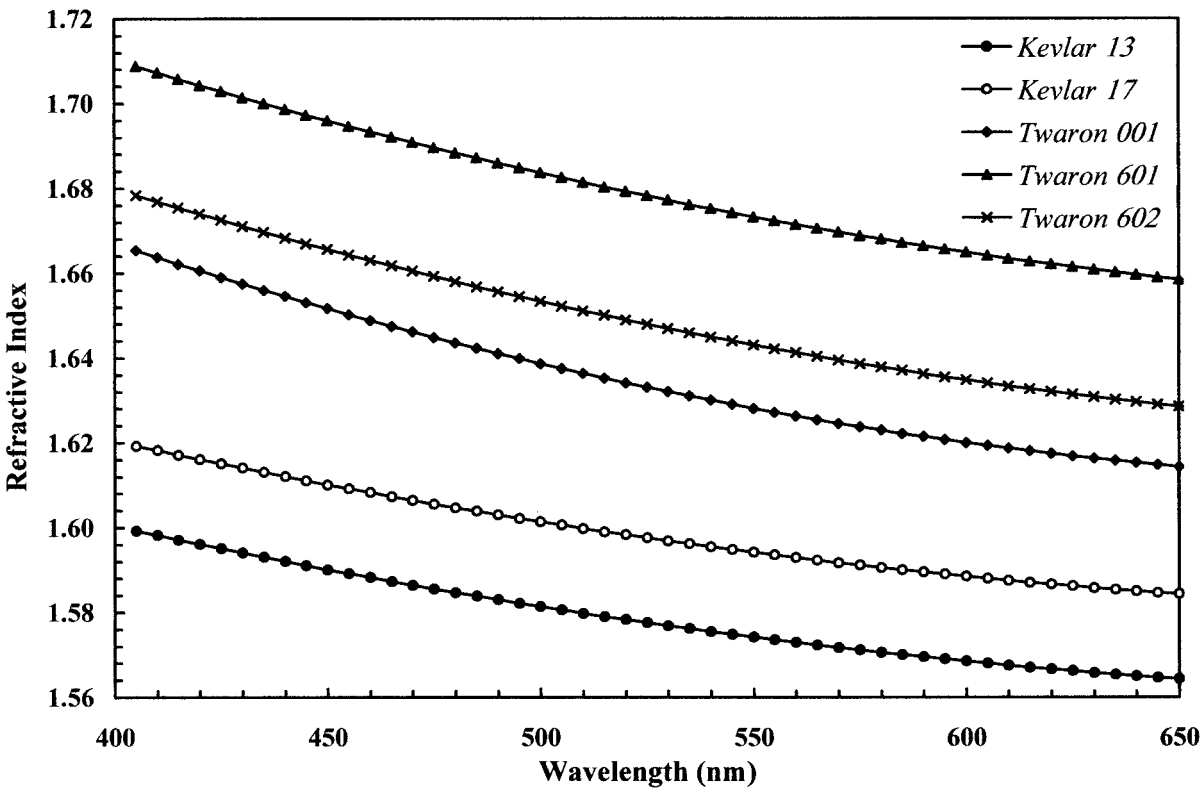
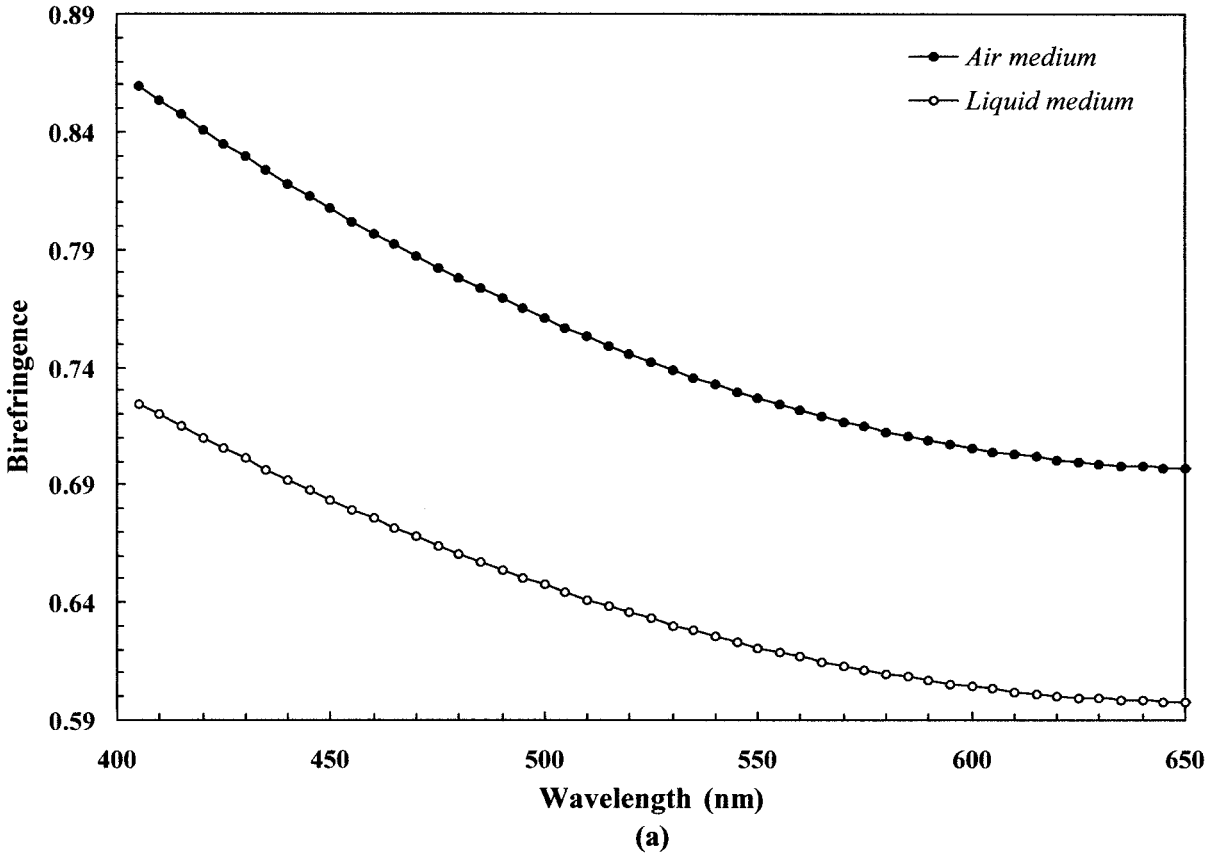


Figure 8 The spectral dispersion curves of PPT fibers for light vibrating perpendicular to the fiber axis.



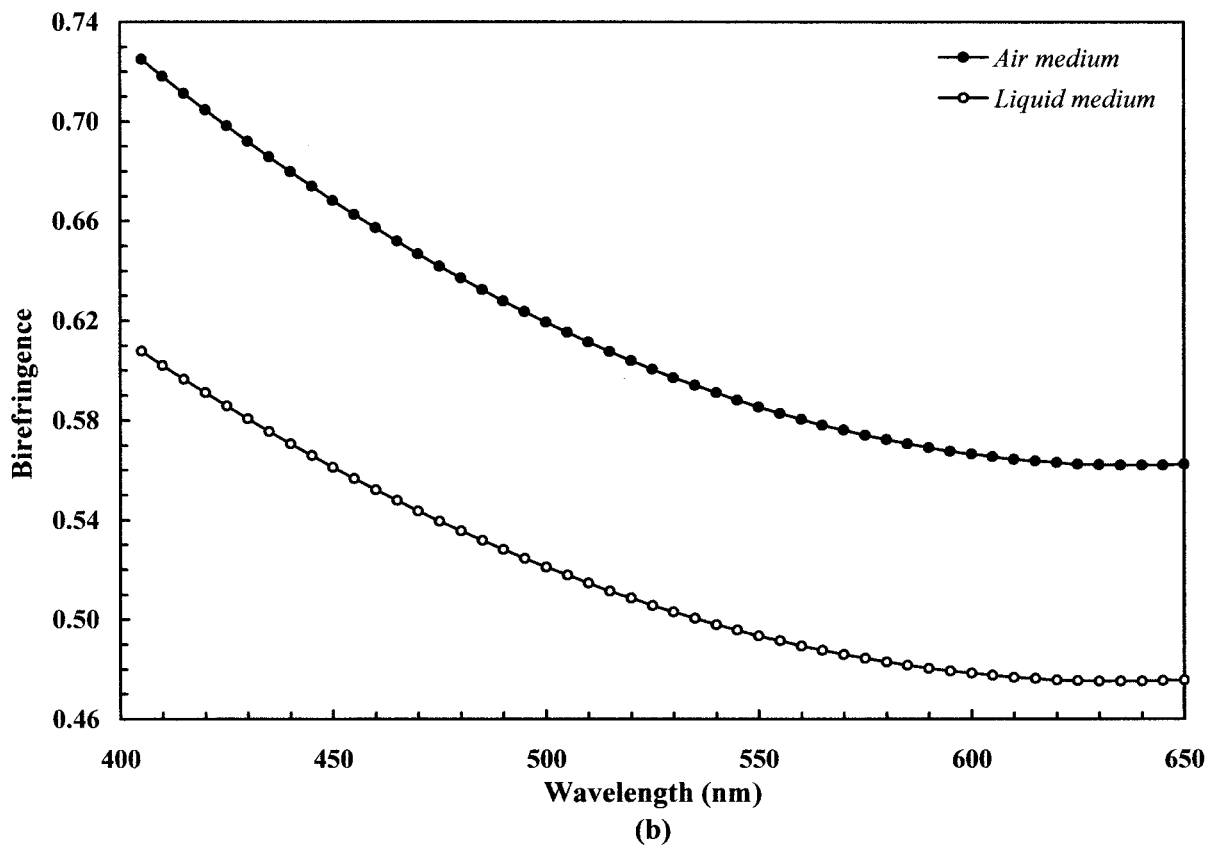
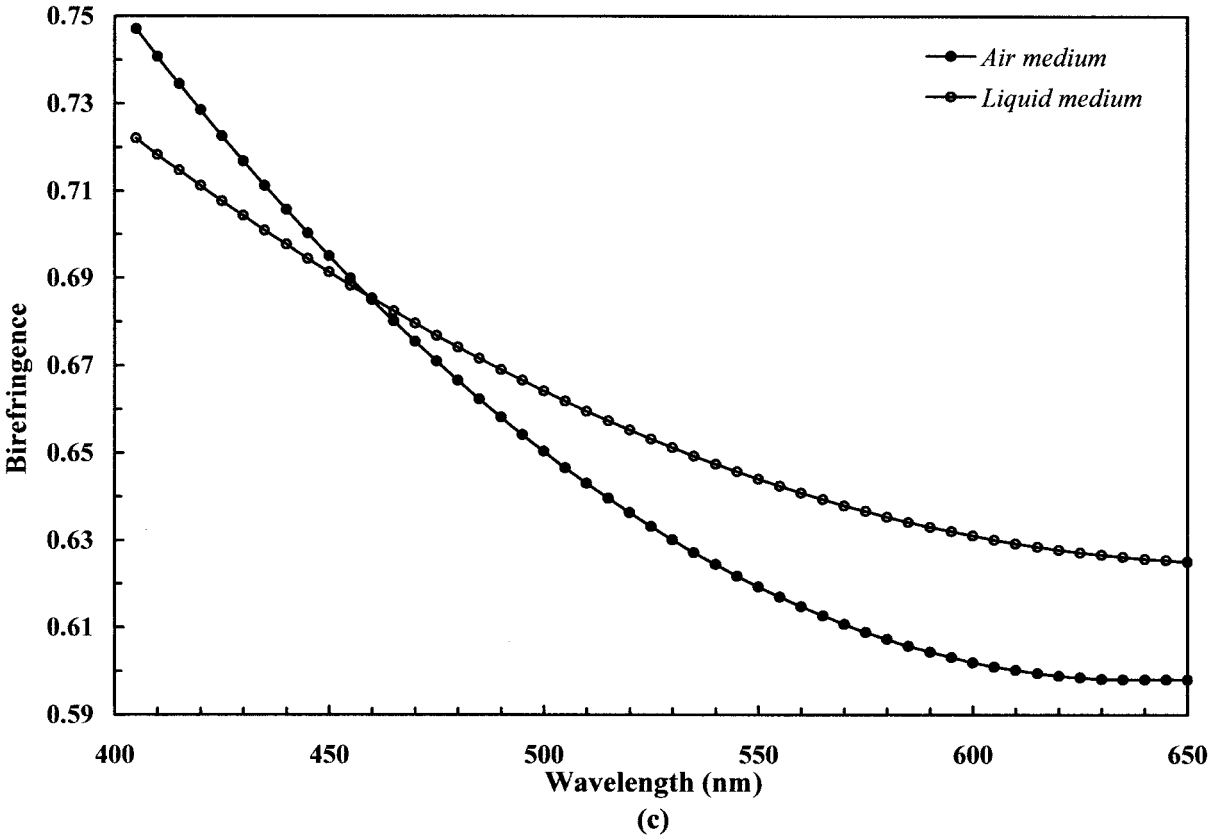


Figure 9 The spectral dispersion curves of birefringence for (a) Kevlar 13, (b) Kevlar 17, (c) Twaron 001, (d) Twaron 601 and (e) Twaron 602 fibers using air and liquid as a surrounding medium to the fiber.



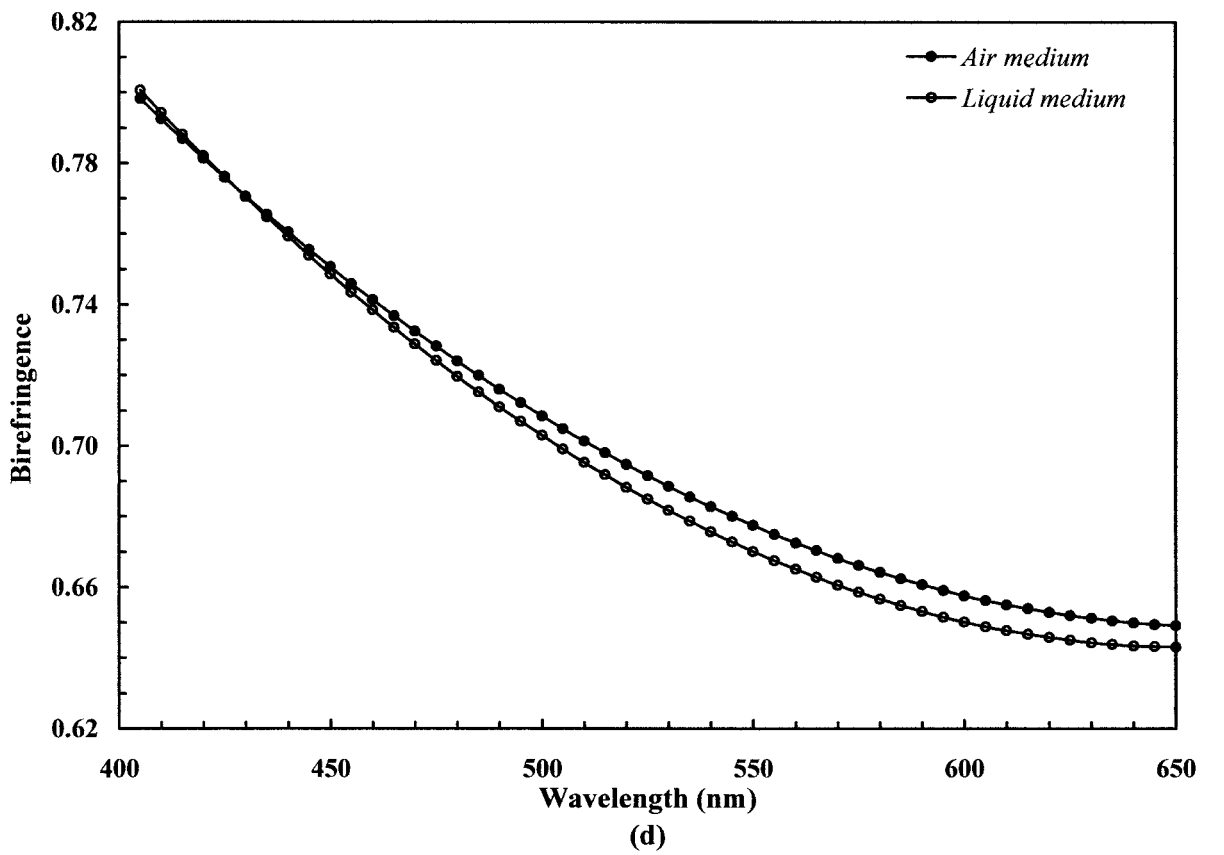


Figure 9 (*Continued from the previous page*)

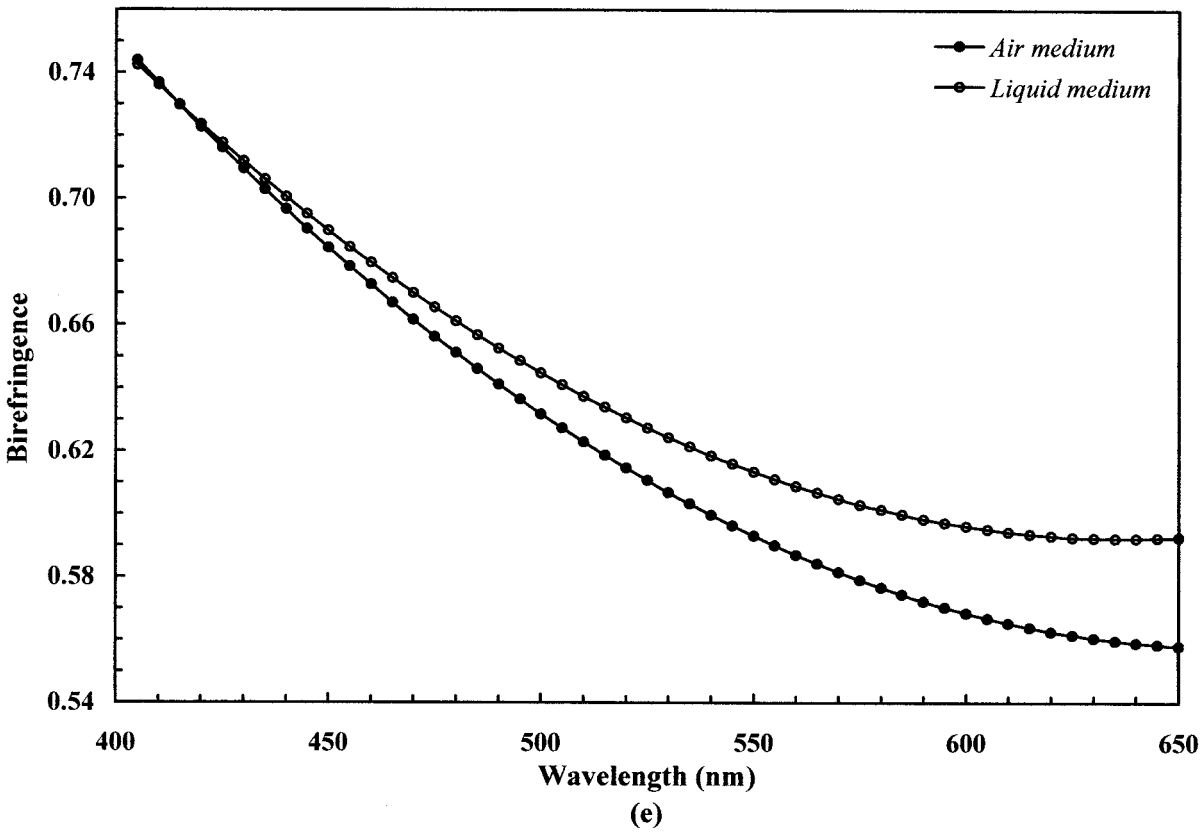


Figure 9 (*Continued from the previous page*)

microscope and the transmission electron microscope via the replication technique (to be published).

The pleat spacing of Kevlar 13 is found to be about 856 nm, as calculated from Figure 4(a); 685 nm from Figure 4(c) and 571 nm from Figure 4(b). However, the pleat spacing of Kevlar 17 is found to be about 1176 nm when calculated from Figure 5(a), 664 nm from Figure 5(b) and 553 nm from Figure 5(c). From these results, one can conclude that the pleat spacing of Kevlar fiber decreases towards the core, and variations are revealed as the etchant attacks down into the fiber. This is possible in spite of the fact that the time of etching is constant, because the fibers were buried at different levels inside the embedding polymer. More detailed electron micrographs (to be published) also show the same skin-core variation. Both Kevlar and Twaron fibers have high mechanical strength, although they have very different kinds of internal pleats or fibrillar structure. Kevlar fibers are also known to be more highly oriented than Twaron, but even on this basis Raman studies under tension have indicated that the differences in morphology between the two types do not give rise to a corresponding difference in mechanical behavior.[24–26] Even if there is a relationship to be found between mechanical properties and pleat period in Kevlar, the very different structure of Twaron indicates that this relationship is not the main determinant of properties.

Kevlar and Twaron fibers are highly anisotropic materials. The variations in the individual refractive indices with wavelength of these fibers for light vibrating parallel and perpendicular to the fiber axis follow very similar curves, which are shown in Figures (7) and (8), respectively. Therefore, the difference between them, the birefringence B, remains substantially the same through the visible spectrum, as shown in Figure (9). PPT fibers absorbs the surrounding liquid, which may change the optical properties of Kevlar fibers Fig. 9(a,b) much more than those of Twaron fibers (Fig. 9(c-e)). This implies some swellability, or more likely porosity, such as that revealed by Dobb et al. using hydrogen sulfide followed by silver nitrate to stain the outer regions of Kevlar fibers.[27]

CONCLUSIONS

The investigation of Kevlar and Twaron fibers under the optical transmission polarizing microscope showed alternately bright and dark interference fringes due to the alternating variation of the fiber thickness along its axis. In addition, this investigation illustrated a periodic pleat structure for the fibers.

Kevlar and Twaron fibers were etched and investigated under a Nomarski differential interference contrast microscope. The two Kevlar fibers were similar and distinct from Twaron fibers. This examination

confirmed that Kevlar fiber has a periodic pleat structure, with some skin-core variation. Twaron fibers showed individual structures with longitudinal fibrillar texture dominating any pleat structure.

The VAWI technique permits rapid determination of the spectral dispersion of refractive indices and birefringence of polymeric and other textile fibers, without the need to use an immersion liquid. The result of this technique indicated that Kevlar and Twaron fibers have ordinary spectral dispersion curves, similar to other anisotropic materials. The absorption of fibers to the immersion liquid changes the optical properties of Kevlar fiber much more than those of Twaron fiber.

I would like to express my thanks to Prof D. C. Bassett, head of the Reading Polymer Science Center; the J. J. Thomson Physical Laboratory; the University of Reading; Reading RG6 6AF, UK for providing samples. My deep gratitude is due to Prof A.A. Hamza, Professor of Optics, Department of Physics, Faculty of Science, University of Mansoura, Mansoura, Egypt, for guidance and illuminating discussion. I would like to thank Mr. R. H. Olley, the J. J. Thomson Physical Laboratory, the University of Reading, Reading RG6 6AF, UK for the fruitful discussion.

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