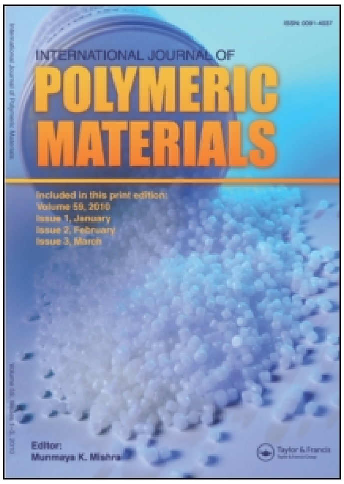

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Interferometric Determination of Structural Properties of PEN Highly Oriented Fiber

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Some optical and structural properties of Poly(ethylene naphthalate-2.6-dicarboxylate), PEN, highly oriented fiber was determined using an automatic variable wavelength interferometric, VAWI, technique. This technique is commonly used jointly with the double refracting polarizing interference microscope designed by Pluta. The microscope was used in two different positions, the subtractive position for determining the spectral dispersion curves of the birefringence and the crossed position for determining the spectral dispersion curves of the refractive indices. The resulting data are utilized to calculate some dispersion and structural parameters such as Cauchy's constants, natural wavelength, dispersion energy, oscillation energy, polarizability per unit volume, dielectric constant, dielectric susceptibility, optical orientation function, and the orientation angle. Microinterferograms are given for illustration.

Keywords: birefringence, dispersion, poly(ethylene naphthalate-2.6-dicarboxylate) (PEN), VAWI-technique

INTRODUCTION

During the past decade, increasing environmental awareness, new global agreements, and international governmental policy and

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regulations have been the driving force behind renewed interest in polymer fiber [1]. Synthetic fibers manufactured from polymers exhibit specific optical properties, which reflect the internal structure and physical behavior of the fiber. The refractive indices and birefringence are generally accepted as a good indicator of molecular orientation, structural homogeneity, polarizability, and other structural properties that describe the functional behavior of the manufactured fibers.

The mechanical properties of polymer fibers are founded on the concept of molecular orientation [2]. The molecular orientation, alignment, and their control become key issues in many applications of polymers to realistic optoelectronic and photonic devices [3]. A wide variety of polymer applications depend on the change of its molecular orientation, such as sensors, high-frequency transducers, nonlinear optical polymers designed for frequency doubling or for electro optical modulation, and polymer optical recording [4]. Also, the investigation of dielectric properties is one of the most conventional and sensitive methods of studying polymer structure [5].

Poly(ethylene naphthalate-2, 6-dicarboxylate), PEN, has appeared as a competitive polymer for applications requiring improved performance in terms of thermal stability and dielectric properties. Its mechanical properties, glass transition temperature, and melting point are higher than those of poly(ethylene terephthalate), PET, because PEN has a naphthaline ring instead of the benzene ring in PET, which is widely used in industry [6–7]. Carr et al. [8] described the experimental spinning and drawing conditions to produce uniform, large diameter PEN monofilaments with high modulus and strength. Huijts and Peters [9] used polarized Raman spectroscopy to obtain the relation between the molecular orientation and birefringence of these fibers.

Microinterferometry has been recognized to be a useful tool in fiber science [10–12]. A detailed survey of the investigators, methods, and techniques of microinterferometry applied to fibrous materials is given [2]. The variable wavelength interferometric method, VAWI, reported by Pluta [13] is especially recommended for studying the spectral dispersion for the birefringence and/or the refractive indices of highly oriented textile fibers. This technique has been modified to be suitable for fully automatic measurements [14]. Hamza et al. [15–16] used the VAWI method to determine the spectral dispersion curves of polypropylene and highly oriented fibers. Also, Sokkar and El-Bakary [17] used this method to determine the refractive index profile of highly oriented fibers. El-Bakary [18] determined the radial structural properties and spectral dispersion curves of PEEK fibers.

In the present work, poly(ethylene 2, 6-naphthalate-dicarboxylate) 1000 denier/248 filaments, PEN-Q50M4; (PEN) PEN highly oriented fibers from Teijin Japan were studied using the automatic variable wavelength interferometric technique, VAWI. The spectral dispersion curves of the refractive indices and birefringence and the dispersion parameters of PEN fibers were measured. The resulting data are utilized to calculate the spectral dispersion and some structural parameters of the polymer material such as Cauchy's constants, natural wavelength, the dispersion energy, oscillation energy, polarizability per unit volume, dielectric constant, electric susceptibility, optical orientation function, and optical orientation angle of PEN fibers.

THEORETICAL CONSIDERATIONS

The Refractive Indices and Birefringence

The measurements of the refractive indices and birefringence of the fiber material can be considered as keys for determining their structural properties using interferometric techniques. Variable wavelength interferometry [12], VAWI, is a method using highly monochromatic light of continuously variable wavelength. It is a method commonly used, jointly with the double refracting polarizing interference Pluta microscope [19–20] for measuring the refractive indices of the fibers using the following equation [21]:

$$\delta_s^{\parallel} = (n_s^{\parallel} - n_s^{\perp})t = (m_l^{\parallel} + q_s)\lambda_s^{\parallel} \tag{1}$$

where $\delta_s^{\parallel}$ are the optical path differences for light vibrating parallel to the fiber axis. The subscript s denotes the coincidence number, q_S is the increment of the initial interference order $m_1 \cdot t$ is the fiber thickness and n_s^1 is the refractive index of the immersion liquid. An analogue formula can be presented for the light vibrating perpendicular to the fiber axis. Using Eq. 1 the spectral dispersion curves of the refractive indices $n^{\parallel}$ and $n^{\perp}$ can be obtained. The isotropic refractive index, which is an average for a highly oriented fiber, can be calculated from the following equation [22]:

$$n_{iso} = \frac{n^{\parallel} + 2n^{\perp}}{3} \tag{2}$$

The birefringence Δn of the fiber material is given by the following equation [21]:

$$\delta_s = \Delta n_s t = (m_1 + q_s)\lambda_s \tag{3}$$

The variation of the refractive index of the fiber material with the wavelength can be written from the known Cauchy's dispersion relation [23]:

$$n(\lambda) = A + \frac{B}{\lambda^2} \quad (4)$$

where $n(\lambda)$ is the refractive index at a given wavelength λ, A and B are constants dependent on the fiber material and called Cauchy's constants. Using these constants, the natural wavelength of the fiber material λ_n is given by reference [24]:

$$\lambda_n = \left(\frac{2AB}{A^2 - 1}\right)^{1/2} \quad (5)$$

Also, the dependence of the refractive index n of the fiber on the wavelength λ of the transmitted photon is described to a good approximation by a Sellmeir's equation for a single oscillator of the form [25]:

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} + \frac{E^2}{E_d E_o} \quad (6)$$

where E_o is the average energy gap or oscillation energy, E is the photon energy, and E_d is the dispersion energy.

The Polarizability Per Unite Volume and Dielectric Properties

The measured values of the refractive indices $n^{\parallel}$, $n^{\perp}$, and n_{iso} of the fiber material at different wavelengths are utilized to show the variation of the values of polarizabilities per unit volume $P^{\parallel}$, $P^{\perp}$, and P_{iso} with the wavelength, by using the Lorantz-Lorenz equation [22]:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} P \quad (7)$$

The following relation [26] gives the dielectric constant ϵ:

$$\epsilon^{\parallel} = n^{\parallel 2} \quad (8)$$

Analogous formulae for $n^{\perp}$ and n_{iso} can be given. When using the index of refraction n_{iso} the direct current dielectric constant ϵ_{dc} can be obtained at the wavelength of infinity, so that Eq. 8 can be rewritten as [26]:

$$\epsilon_{dc} = n_{iso}^2 \quad (\text{at } \lambda = \infty) \quad (9)$$

Plotting $1/(n_{iso}^2 - 1)$ versus $(1/\lambda^2)$, a linear relationship is obtained from which the direct current dielectric constant ϵ_{dc} can be calculated [24,27].

The dielectric susceptibility η is related to the dielectric constant ϵ by the following equation [26]:

$$\eta = \frac{\epsilon - 1}{4\pi} \tag{10}$$

Optical Orientation Function and Orientation Angle

For a highly oriented fiber where the molecules are considered to be aligned with a preferred direction but only randomly arranged in the transverse section, the optical properties of the system can be specified by only two refractive indices, $n^{\parallel}$ parallel to the fiber and $n^{\perp}$ perpendicular to the fiber axis. The molecular orientation can be specified by the birefringence, which is the difference between the two refractive indices. The Hermans orientation factor $F(\theta)$ is then related to the birefringence by the relation [27]:

$$F(\theta) = \frac{n^{\parallel} - n^{\perp}}{\Delta_o} \tag{11}$$

where Δ_o is the intrinsic maximum birefringence that corresponds to the case where all the molecules are perfectly aligned. The optical orientation angle θ can be found using Hermans orientation factor form the following equation [28]:

$$\theta = \sin^{-1}\left(\frac{2}{3}(1 - F(\theta))\right)^{1/2} \tag{12}$$

where θ is the angle between the polymer chain and the fiber axis. If all polymer chains were aligned parallel to the fiber axis, the optical orientation factor $F(\theta)$ would be 1. For isotropic system where there is no orientation $F(\theta)$ would be 0.

EXPERIMENTAL TECHNIQUE

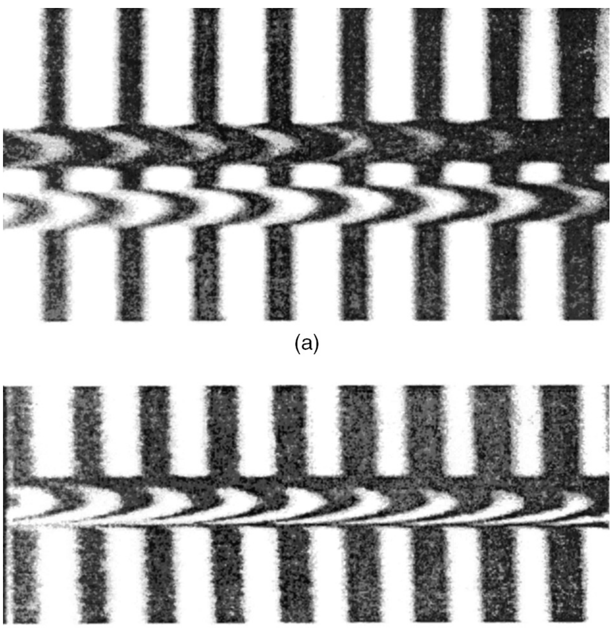
An automatic computer-aided micro-interferometer [14] was used. This technique is specially designed to measure and study the spectral dispersion of the refractive indices of fibrous material using VAWI technique. The main part of the automatic optical system is the Biolar PI micro-interferometer [19–20] that is fitted with a Halogen lamp (12 V/100 watt) as highly monochromatic light source, wedge interference filter, stepper motor controller, PC computer with framegrabber, CCD camera, and image display monitor. The image is grabbed and digitized using the framgrabber digitizer installed in the PC. The contrast of the fringes is optimized by adjusting the intensity of the interference field with the width of the condenser slit. The measurements using this technique are controlled by using image analysis software program.

MEASUREMENTS, RESULTS AND DISCUSSIONS

The Fiber Thickness and Refractive Indices

The tested sample of PEN fibers is placed on the microscope stage and the micro-interferometer is adjusted in subtractive position [14] for automatic measurement of the fiber thickness. The average thickness of the tested sample is found to be 19.8 μm.

For the measurements of the spectral dispersion curves of the refractive indices, the micro-interferometer is adjusted in crossed position [14] for obtaining the duplicated images of PEN fiber, one for the parallel direction and the other for the perpendicular direction of the vibrating light. Figure 1a shows the printed microinterferogram taken



(a)

(b)

FIGURE 1 Microinterferograms of duplicated and non-duplicated images of PEN fiber for measuring the (a) refractive indices and (b) birefringence using automatic VAWI technique.

from the image screen of duplicated images for the refractive indices of PEN fiber using automatic VAWI technique. The upper image of the fiber is for the parallel direction of light vibration and the lower image for the perpendicular direction. The microscope is adjusted in subtractive position [14] for obtaining a non-duplicated image of PEN fiber for the automatic measurement of the fiber birefringence. Figure 1(b) shows the printed microinterferogram for non-duplicated image of PEN fiber using automatic VAWI technique.

Figure 2 gives the spectral dispersion curves of refractive indices $n^{\parallel}$, $n^{\perp}$, and n_{iso} and birefringence Δn of PEN highly oriented fiber in the wavelength range from 400 to 620 nm. This shows the normal dispersion behavior of the fiber material. To verify the Cauchy's dispersion formula for PEN fiber we plotted the refractive indices $n^{\parallel}$, $n^{\perp}$, and n_{iso} with the inverse squared wave length $(1/\lambda^2)$ in the same range of wavelengths. Figure 3 illustrates the linear behavior of this relationship. From the slope and the intersect parts of the straight lines, the constants A and B of Cauchy's dispersion formula were calculated and then the natural wavelength of the fiber material as calculated using Eq. 5. The results are given in Table 1. The values of both the constants A and B for the two directions of vibration light

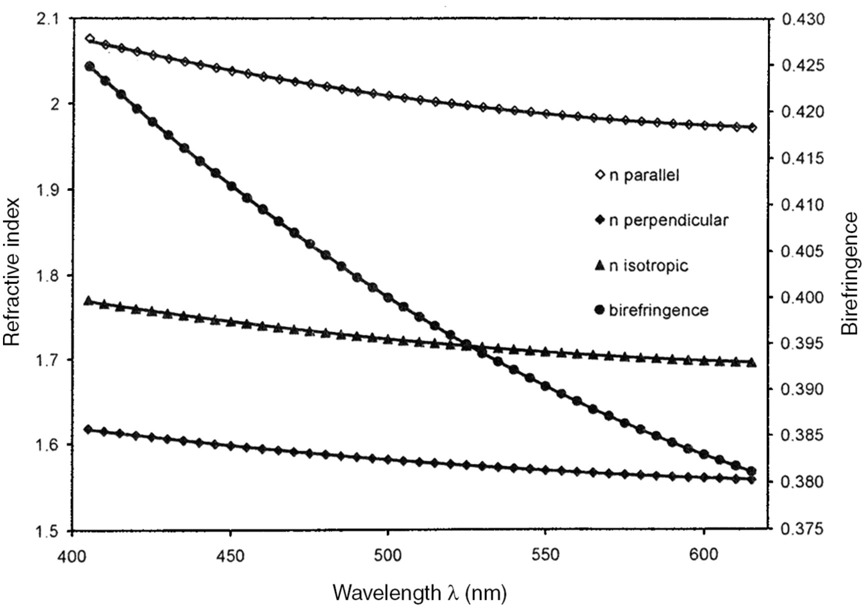


FIGURE 2 The spectral dispersion curves of refractive indices $n^{\parallel}$, $n^{\perp}$, and n_{iso} and birefringence Δn of PEN highly oriented fiber.

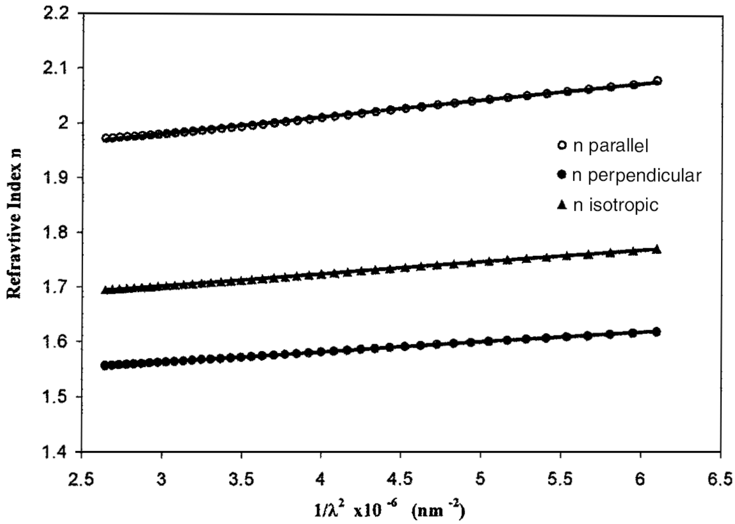


FIGURE 3 The refractive indices $n^{\parallel}$, $n^{\perp}$, and n_{iso} as a function of $1/\lambda^2$ to verify Cauchy's dispersion relation for PEN fiber.

and the isotropic one indicate the high degree of the molecular orientation in the parallel direction of the vibrating light than in the perpendicular direction. The value of the natural wavelength lies in the short-UV region of the spectrum.

The refractive indices vary with the variation of the wavelength of the incident light beam because of the refraction effects produced by the interaction between light and matter. This gives rise to the oscillation and dispersion properties of the PEN fiber material. To determine the oscillation energy and dispersion energy in the fiber, a relation between $(n^2 - 1)^{-1}$ and the square of the photon energy E^2 was plotted. Straight lines were obtained as shown in Figure 4. From their slopes and intersect parts, the oscillation energy E_o and dispersion energy E_d were calculated. The results are given in

TABLE 1 The Dispersion Parameters of PEN Fiber Using VAWI Technique

	Dispersion parameters				
Direction of the vibrating light	A	$B \times 10^3\,nm^2$	E_d (ev)	E_o (ev)	λ_n nm
Parallel	1.889	30.2	17.674	6.736	210.8
Perpendicular	1.510	17.7	9.057	6.944	204.4
Isotropic state	1.636	21.9	11.747	6.865	206.7

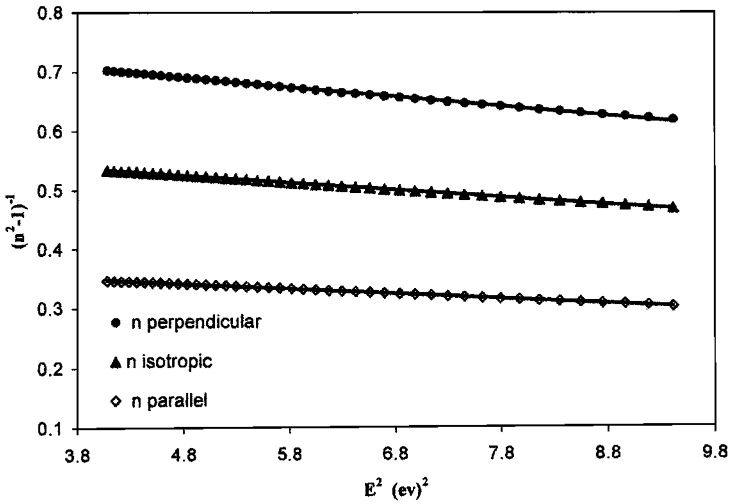


FIGURE 4 The plot of $(n^2-1)^{-1}$ versus the square of photon energy E^2 for PEN fiber.

Table 1. The dispersion energy is called the electronic oscillator strength, which is a measure of the strength of inter-band optical transition; it is related to the charge distribution within each unit cell and related to chemical bonding. It plays an important role in determining the behavior of refractive indices and properly normalizes the interaction potential describing these optical effects. This is due to the relationship between electronic optical properties of the material and its chemical bound [25].

The values of the refractive indices of the polymer depend on the polarizability per unit volume, so that the variation of the refractive index leads to the variation of the polarizability per unit volume. Figure 5 gives the variation of the polarizability per unit volume $P^{\parallel}$, $P^{\perp}$, and P_{iso} with the wavelength of the incident light. Also, the dielectric constants $\epsilon^{\parallel}$, $\epsilon^{\perp}$, and ϵ_{iso} of PEN fiber material and the dielectric susceptibilities $\eta^{\parallel}$, $\eta^{\perp}$, and η_{iso} were calculated using Eq. 8 and 10, respectively, and the dispersion of these quantities are given in Figures 6 and 7. Figure 8 gives the relation between $(n_{iso}^2-1)^{-1}$ and $1/\lambda^2$, from which the d.c. dielectric constant d_{dc} is calculated. It is found to be 2.711.

The optical orientation factor and angles depends on the refractive indices difference or birefringence as shown in Eq. 11, so that the dependence of the refractive indices on the wavelength values leads to a variation of the optical orientation factor and angle with the wavelength. Using the intrinsic birefringence value of PEN fiber

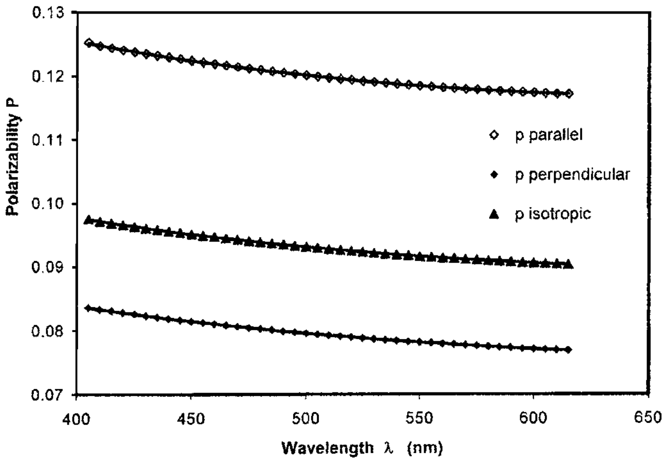


FIGURE 5 The variation of the polarizability per unit volume $P^{\parallel}$, $P^{\perp}$, and P_{iso} with the wavelength of the incident light.

($\Delta_o = 0.426$) [8] and the measurable refractive indices values, the optical orientation factor and angles were calculated using Eq. 11. Figure 9 gives the variation of the optical orientation factor and angle with the wavelength. It is clear from this figure that the optical orientation factor decreased with increasing wavelength whereas the orientation angle increased with increasing wavelength.

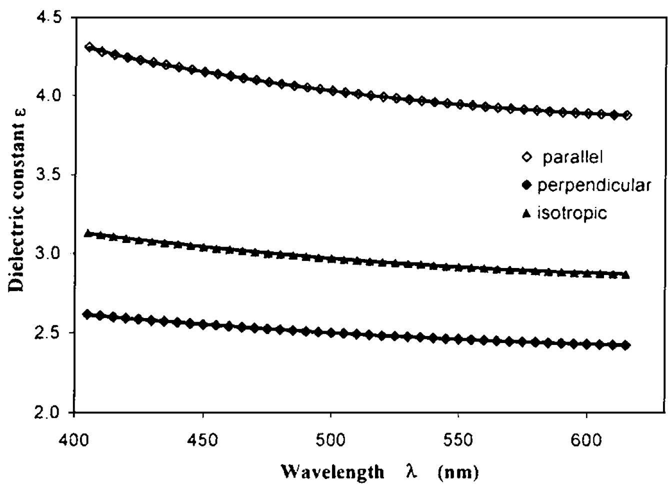


FIGURE 6 The variation of the dielectric constants $\epsilon^{\parallel}$, $\epsilon^{\perp}$, and ϵ_{iso} with the wavelength of the incident light.

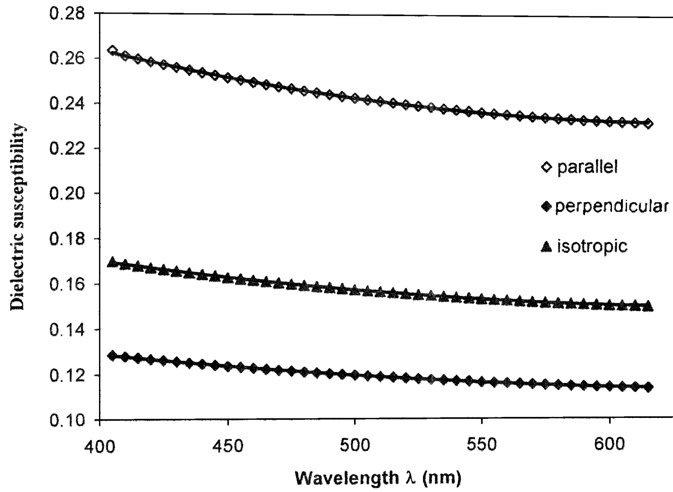


FIGURE 7 The variation of the dielectric susceptibilities $\eta^{\parallel}$, $\eta^{\perp}$, and η_{iso} with the wavelength of the incident light.

The present work emphasizes that application of the VAWI technique is suitable for studying the optical properties of highly oriented fibers. This technique enables the spectral dispersion curves of the refractive indices ($n^{\parallel}$, $n^{\perp}$, and n_{iso}) to be determined quickly. The accuracy of the measurement of the refractive index n is about 0.1%. Also, it is 0.5 nm for the wavelength λ using this technique

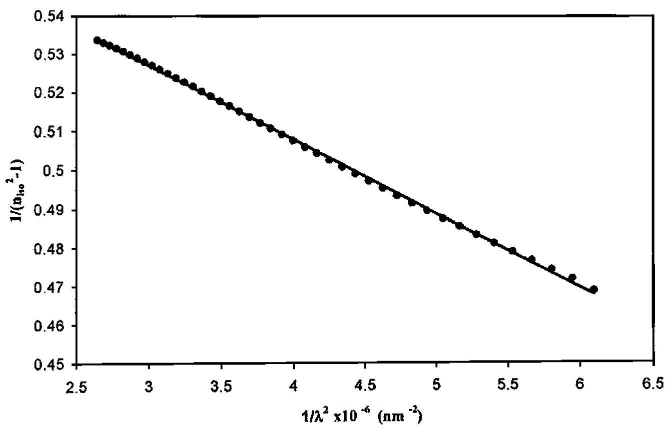


FIGURE 8 The relation between $(n_{\mathrm{iso}}^2 - 1)^{-1}$ and $1/\lambda^2$ for the d.c. dielectric constant d_{dc} calculation.

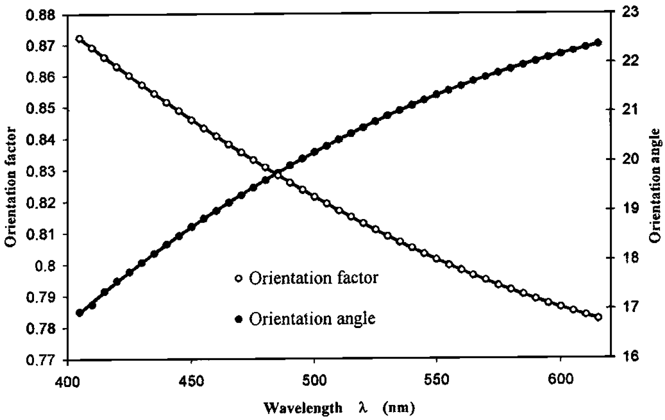


FIGURE 9 The variation of the optical orientation factor and angle of PEN fiber material with the wavelength.

[19]. Moreover, this method should be particularly useful and important for structural investigation of tested fiber.

CONCLUSIONS

From the measurements carried out in the present work using automatic VAWI technique for PEN fiber, the following conclusions may be considered:

1. The use of the VAWI technique verifies the Cauchy's dispersion formula and determines their constants, which relate the molecular arrangement of PEN fiber with the wavelength of the incident light beam, from the plot of the refractive index n versus $1/\lambda^2$.
2. The plot $(n^2 - 1)^{-1}$ as a function of squared photon energy E^2, enables us to determine the oscillation energy, E_o and the dispersion energy, E_d, according to Eq. 6.
3. From the plot $(n_{iso}^2 - 1)^{-1}$ and λ^{-2}, the d.c. dielectric constant d_{dc} is calculated and it is found to be 2.711.
4. Measurements of the optical orientation factor, optical orientation angle, and polarizability per unit volume throw light on the axial orientation of the molecules and hence in the structure order of PEN fiber material.

Finally, the experimental results and calculations in this article confirm the dispersion of some structural properties of PEN fibers. These results are useful for industry and human's end use. The VAWI technique is a suitable and promising technique for accurate determination of optical and structural properties of PEN fibers.

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