Opto-Thermal Properties Of Fibers: XVII. Structure Characterization Of Cold Drawn Boiled Viscose Fibers

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ABSTRACT: A two-beam interferometric method is used to study the change of optical parameters of cold drawn boiled viscose fibers at different times. A stress-strain device conjugated to the Pluta polarizing interference microscope is used to investigate the dynamical behavior of opto-mechanical properties at room temperature. Some structural parameters such as the number of molecules per unit volume, the virtual and isotropic refractive indices, the optical orientation factor and angle, the strain and the stress optical coefficients are evaluated. Some mechanical parameters such as, Young's modules, elastic shear modules and the compressibility are calculated over different strain values. Also the number of network chain per unit volume N_c , work per unit volume W, average work per chains W', reduction in entropy ΔS , and the optical configuration parameter $\Delta \alpha$ are determined. Also calculation of the constants of Moony-Rivilin equation are given. A systematic study over different wavelengths range extending from 405 to 590 nm was carried out to obtain the dielectric constant at infinity. The obtained results clarify that new reorientations occurred due to cold drawing at different conditions. Empirical formula is suggested to correlate the change in Δn , $f(\theta)$, W, W', A, θ , and N_c with different draw ratio, and its constants were determined. Microinterferograms and curves are given for illustrations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1185-1201, 1999

Key words: interferometry; viscose fibers; birefringence; optical configuration; orientation

INTRODUCTION

Optical anisotropy produced in fibers by stretching gives valuable information for characterization of these fibers on the molecular level. An analysis of the relation between the birefringences and the draw ratios of some synthetic fibers has appeared in extensive publications. The orientation can be produced by either hot stretching of a molten polymer followed by rapidly cooling of the melt, by cold drawing, or by cold rolling. Cold drawing manifests itself as a necking of the polymer during stretching. Cold drawing after the yield point means that there must be a strain hardening process; otherwise, the material would break without drawing at the reduced cross section where necking took place. The strain hardening generally results from molecular orientation, which increases the modules and tensile strength. The draw ratios are functions of temperature, orientation, and other variables. On further stretching of the cold drawn polymer, the stress generally rapidly increases and failure soon occurs. Oriented polymers have birefringence: the refractive indices along the orientation and at right angle to it are different. When this

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difference (Δn) is larger, the segments are oriented more in the direction of force action.^{1–9}

In the present work a modified microstrain device designed¹⁰ earlier and modified¹¹ was used in conjunction with a double-beam interference microscope to study the optical and mechanical parameters produced in viscose fibers (viscose rayon filament, Misr Co. of Artificial Silk, Egypt) under different conditions. The variations of refractive indices and birefringence by different stresses were studied. The resulting data were utilized to calculate the strain optical coefficient, stress optical coefficient, optical orientation function, orientation angle, Poisson's ratio, and the virtual refractive index. Also determined were the constants of Moony–Rivlin equation, $(\Delta \alpha/3\alpha_0)$ the electric polarizability polymer structure constant, and other optical and mechanical parameters.

Theoretical Consideration

The totally duplicated image of the examined fibers by the double-beam interference Pluta microscope was used to measure the mean refractive indices of the fibers. Measuring the area under the fringe shift F, the difference between the refractive indices of the fiber and that of immersion liquid was used to overcome the irregularity of fibers. The following expression^{9,12} was used to determine the refractive indices of the fiber which has irregular cross section and deformed during the drawing process.

$$n^{\parallel} = n_L + (F^{\parallel} D/A) \ (\lambda/h) \tag{1}$$

with an analogous formula for n^{\perp} . n_L is the liquid refractive index, h the interfringe spacing, D the draw ratio, A the cross section area of undrawn sample, A/D the cross section area of drawn sample, F^{\parallel} the area under fringe shift, and λ the wavelength of the source used. n^{\parallel} and n^{\perp} are the refractive indices of the fiber with light vibrating along and across the axis of the fiber. Equation 1 can be applied, fairly, to interferograms of viscose fibers that undergo a successive deformation during the drawing process.⁹ In addition to measuring both n^{\parallel} and n^{\perp} , the microscope can be adjusted for measuring birefringence directly using the following equation:

$$\Delta n = F \frac{D}{A} \frac{\lambda}{h} \tag{2}$$

Mechanical Properties

The applied stress can be obtained, using the general equation

$$\sigma = \frac{mg}{A} \tag{3}$$

Young's modules was calculated from the following equation:

$$E = \sigma/\varepsilon \tag{4}$$

where ε is the strain = D - 1. The strain optical coefficient is given from the following equation⁸:

$$C_{\varepsilon} = \frac{d(\Delta n)}{d\varepsilon}$$
(5)

where the change in birefringence is $d(\Delta n)$ and the corresponding change in strain is $d\varepsilon$. Poisson's ratio μ given from the following equation:

$$dr/r = -\mu \ dL/L \tag{6}$$

where dr is the change in radius (r) and dL is the change in fiber length (L). The elastic shear module G is given using the following equation¹⁴:

$$G = \frac{E}{2(1+\mu)} \tag{7}$$

where E is Young's modules. The compressibility¹³ is given by



Plate 1 The resultant cross section of irregular viscose fiber.

D	3	$\sigma \times 10^{10} $ (Pa)	$E \times 10^{10} $ (Pa)	$C_{arepsilon} imes 10^{-3}$	$C_S \ imes 10^{-10} \ (\mathrm{Pa})^{-1}$	μ	$G imes 10^{10} ext{(Pa)}$	$\begin{array}{c} \chi \ 10^{-10} \ (\mathrm{Pa})^{-1} \end{array}$
				Unboiled Sar	nple			
1.00	0	_	_	_	_		_	
1.04	0.04	3.54	88.5	25	1.27	0.48	29.89	1.35
1.08	0.08	5.67	70.87	17	0.917	0.46	24.27	3.38
1.16	0.16	7.81	48.81	8	0.755	0.43	17.06	8.60
1.20	0.2	9.46	47.30	15	0.687	0.41	16.77	11.41
			Sa	mple Boiled fo	r 15 min			
1.00	0	_	_	_	_	_	_	
1.04	0.04	2.73	68.25	17	1.72	0.48	23.05	1.76
1.08	0.08	3.54	44.25	20	1.55	0.46	15.15	5.42
1.16	0.16	4.56	28.5	8	1.36	0.43	9.96	14.70
1.20	0.2	5.52	27.6	10	1.19	0.41	9.78	19.56
			Sa	mple Boiled fo	r 30 min			
1.00	0	_	_	_	_	_	_	
1.04	0.04	2.73	68.25	20	1.86	0.48	23.05	1.76
1.08	0.08	4.25	53.12	27	1.46	0.46	18.19	4.52
1.16	0.16	7.62	47.62	10	0.918	0.43	16.65	8.82
1.20	0.2	9.08	45.4	7	0.804	0.41	16.10	11.89
			Sa	mple Boiled fo	r 60 min			
1.00	0	_		_	_	_	_	_
1.04	0.04	3.54	88.5	20	1.49	0.48	29.89	1.35
1.08	0.08	5.67	70.87	25	1.11	0.46	24.27	3.38
1.16	0.16	6.38	39.87	5	1.05	0.43	13.94	10.53
1.20	0.2	7.56	37.80	10	0.94	0.41	13.40	14.28

 Table I
 Values of Draw Ratio, Strain, Stress, Young's Modulus, Strain Optical Coefficient, Stress

 Optical Coefficient, Poisson's Ratio, Elastic Shear Modulus, and Compressibility

$$\chi = \frac{3(1-2\mu)}{E} \tag{8}$$

For uniaxial tensile stress, the birefringence and the retractive stress are related by the equation¹⁴

$$(n^{\parallel} - n^{\perp}) = C_S \sigma \tag{9}$$

The constant C_s is called the stress-optical coefficient. Its value is dependent on the chemical structure of the polymer, and it decreases as the draw ratio is increased.

Application of Continuum Theories of Rubber Elasticity

The rubber elasticity experiments were performed to determine the number-average molecular weight between network junctions.¹⁵ Rubberlike force-extension curves were obtained for all filaments boiled and unboiled. Treatment of stress–strain relationship for deformable materials was carried out without the assumption of any specific molecular model. Arising from this one widely employed equation (Mooney–Rivlin)¹⁶

$$\sigma/(D - D^{-2}) = 2c_1 + 2c_2 D^{-1} \tag{10}$$

plots of $[\sigma/(D - D^{-2})]$ and 1/D are found to be linear, especially at low elongation. The intercept on the $D^{-1} = 0$ axis yields $2C_1$, and the slope yields $2C_2$. The second term was attributed to energy dissipation resulting from chain interactions during deformation, and in conformity with



Figure 1 (a)–(d) The relationships among the draw ratio D and E, G, χ , and C_S for the unboiled sample and samples boiled for 15, 30, and 60 min, respectively.

this view C_2 becomes zero when the elastomer is swollen by solvents.¹⁶

Because the stress is related to the elongation by

$$\sigma = N_c K T \left(D - D^{-2} \right) \tag{11}$$

where σ is the stress, K is the Boltzman's constant, T is the absolute temperature, and N_c is the number of network chains per unit volume given from the following equation:

$$N_c = \frac{\sigma}{3KT} \left[\varepsilon + \frac{1}{3} \frac{\varepsilon^3}{1+\varepsilon} \right]^{-1}$$
(12)

Also the elongation leads to a reduction in the entropy ΔS by the following equation:

$$\Delta S = -\frac{1}{2} K N_c \left[(1+\varepsilon)^2 + \frac{2}{(1+\varepsilon)} - 3 \right] \quad (13)$$

The average work per chain for a collection of chains will depend on the distribution of chainend distances and is obtained by the following equation¹⁷:

$$W' = \frac{3K T}{2} \left[\frac{1}{3} (D^2 - D^{-1}) + (D^{-1} - 1) \right] \quad (14)$$



Figure 2 The relationships among $[\sigma/(D - D^{-2})]$ and D^{-1} for unboiled sample.

For a collection of chains containing N_c chains per unit volume, the work per unit volume W is given by

$$W = \frac{N_c K T}{2} \left[(D^2 - D^{-1}) + 3(D^{-1} - 1) \right] \quad (15)$$

The storable, elastic energy of the network is only a function of the strain invariant. It can be represented by the following equations for uniaxial elongation:

$$W'' = C_1(D^2 + (2/D) - 3) + C_2(D^{-2} + 2D^{-3})$$
 (16)

and

$$\sigma = \frac{dW}{dD} = C_1(2D - 2D^{-2}) + C_2(2 - 2D^{-3}) \quad (17)$$

or

$$\sigma = 2(C_1 + (C_2/D)) (D - D^{-2})$$
(18)

Equation (18) is the well-known Mooney–Rivlin equation. A plot of the reduced stress $\sigma/2$ ($D - D^{-2}$) as a function of reciprocal elongation D^{-1} gives straight line whose slope is C_2 and whose intercept with the ordinate is C_1 . In practice the constants C_1 proved to be a useful measure of the crosslink density.

Stress-Optical Coefficient

The value of the stress-optical coefficient C_S is dependent on the chemical structure of the polymer. Also the value of this coefficient depends solely on the mean refractive index and the optical anisotropy of the random link as seen from the following equation¹⁸:

$$\frac{\Delta n}{\sigma} = C_S = \frac{2\pi}{45 \ K \ T} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \left(b_1 - b_2\right) \quad (19)$$

where \bar{n} is the average refractive index and b_1 and b_2 are the polarizabilities along and across the axes of such units.

From the above equation it can be seen that birefringence in elastomers is proportional to the applied stress.

Calculation of the Optical Configuration Parameter

The optical configuration parameter $\Delta \alpha$ is related to the stress-optical coefficient C_S by the following equation¹⁸:

$$\Delta \alpha = \frac{(45 \ K \ T \ C_S / 2 \ \pi) \ \bar{n}}{(\bar{n}^2 + 2)^2} \tag{20}$$

where $\Delta \alpha = b_1 - b_2$ from eq. (19) and *n* is the refractive index of the network. Values of $\Delta \alpha$ at different values of *n* and C_S are summarized in the tables.

The values obtained for n^{\parallel} and n^{\perp} were utilized in calculating the following optical parameters: the polarizabilities per unit volume P^{\parallel} and P^{\perp} , the isotropic polarizability P_0 , the isotropic refractive index n_{iso} . Other optical parameters are given later on, where

$$P^{\parallel} = \frac{3}{4\pi} \frac{(n^{\parallel^2} - 1)}{(n^{\parallel^2} + 2)}$$
(21)

Table II Constants C_1 and C_2 of Mooney-Rivlin Equation

Type of Sample	$C_1 imes 10^7$	$C_2 imes 10^7$
Unboiled	-31.67	48.63
Boiled for 15 min	-35.79	48.73
Boiled for 30 min	-7.89	19.93
Boiled for 60 min	-47.62	65.49

D	$N_c imes 10^{30}$	$W imes 10^{6} \ { m (J)}$	$W' imes rac{10^{-23}}{({ m J})}$	$\Delta S imes 10^7 \ (\mathrm{JK}^{-1})$	$(b_1 - b_2) \ imes 10^{-25} \ ({ m cm}^3)$	$\lambdalpha \ imes 10^{-25} \ ({ m cm}^3)$
			Unboiled Sample			
1.00	_	_		_	_	_
1.04	71.66	.88	1.234	-2.3	2.99	2.99
1.08	57.31	2.12	3.703	-7.2	2.19	2.19
1.16	39.26	5.33	13.57	-18.8	1.80	1.80
1.20	37.9	7.95	20.98	-27.7	1.64	1.64
		S	Sample Boiled for 15	min		
1.00	_	_	_	_	_	_
1.04	55.27	0.68	1.234	-1.78	4.05	4.05
1.08	35.78	1.32	3.703	-4.49	3.70	3.70
1.16	22.92	3.11	13.57	-11.02	3.25	3.25
1.20	22.11	4.64	20.98	-16.18	2.84	2.84
		S	Sample Boiled for 30	min		
1.00						_
1.04	55.27	0.68	1.234	-1.78	4.38	4.38
1.08	42.95	1.59	3.703	-5.39	3.44	3.44
1.16	38.30	5.2	13.57	-18.43	2.19	2.19
1.20	36.38	7.63	20.98	-26.62	1.92	1.92
		S	Sample Boiled for 60	min		
1.00		_	_	_	_	
1.04	71.66	0.68	1.234	-2.3	3.51	3.51
1.08	57.31	1.59	3.703	-7.2	2.62	2.62
1.16	32.07	4.35	13.57	-15.43	2.51	2.51
1.20	30.28	6.35	20.98	-22.15	2.24	2.24

Table III Values of Number of Network Chain per Unit Volume N_c , Work per Unit Volume W, Average Work per Chains W', Reduction in Entropy ΔS , Polarizabilities along and across the Axes of Unit Chain $b_1 - b_2$, and the Optical Configuration Parameter $\Delta \alpha$

The *n* values were also used to calculate an analogous equation for P^{\perp} . The isotropic polarizability is given by

$$P_0 = \frac{1}{3} \left(P^{\parallel} + 2P^{\perp} \right)$$
 (22)

whereas the isotropic refractive index n_{iso} is given from the following equation:

$$n_{\rm iso} = \frac{1}{3} \left(n^{\parallel} + 2n^{\perp} \right) \tag{23}$$

Also, de Vries¹⁹ defined the invariant refractive index, which he calls the "virtual refractive index," n_v by

$$n_{v} = \sqrt{1 + \frac{3[n_{\parallel}^{2} - 1][n_{\perp}^{2} - 1]}{[n_{\perp}^{2} - 1] + 2[n_{\parallel}^{2} - 1]}}$$
(24)

where the virtual refractive index n_v replaces the isotropic refractive index equation.

The optical orientation function f_{Δ} was measured from the following equation²⁰:

$$f_{\Delta} = \frac{\Delta n_a}{\Delta n_{\max}} \tag{25}$$

where $(\Delta n_{\rm max})$ is the maximum birefringence of a fully oriented fiber. Its value was previously²⁰ determined to be 0.055.



Figure 3 (a)–(d) The relationships among ΔS and draw ratio for all samples.

 $Ward^{21,22}$ studied the average value of the optical orientation function from the following equation:

$$\langle P_2(\theta) \rangle = \frac{\Delta n_a}{\Delta n_{\max}}$$
 (26)

 $\langle P_2 \; (\theta) \rangle$ is related to the polarizabilities $\Phi^\|$ and Φ^\perp by the relation 23



Figure 4 The relationships among the number of network chain per unit volume and the draw ratio for all samples.



Figure 5 (a)–(d) The relationships among work per unit volume and the draw ratio for all samples.

$$\frac{\Phi^{\parallel} - \Phi^{\perp}}{\Phi^{\parallel} + 2\Phi^{\perp}} = \langle P_2(\theta) \rangle P_2(\theta_m)$$
(27)

where $P_2(\theta_m)$ is constant. The values of Φ^{\parallel} and Φ^{\perp} are determined from the following equation due to Stein and Wilkes²⁴:

$$\Phi^{\parallel} = \frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2} \tag{28}$$



Figure 6 The relationships among the average work per chain and the draw ratio.



Plate 2 (a)–(h) Some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position.

The above equation (15) can be written in the form

$$\frac{\Phi^{\parallel} - \Phi^{\perp}}{\Phi^{\parallel} + 2\Phi^{\perp}} = \left[\frac{\Delta\alpha}{3\alpha_0}\right] \langle P_2\left(\theta\right) \rangle \tag{29}$$

where $(\Delta \alpha/3\alpha_0)$ as a quantity depends on the molecular structure and can be obtained from the relation between $P_2(\theta)$ and $[(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})]$, which gives a straight line.

The function f_{θ} is developed in a new approach to the continuum theory of birefringence of oriented polymer²⁵ where

$$f_{\theta} = \frac{n_{1}^{2} n_{2}^{2}}{n_{\parallel}^{2} + n_{\perp}^{2}} \frac{n_{\parallel} + n_{\perp}}{n_{1} + n_{2}} \left(\frac{\Delta n}{\Delta n_{\max}}\right)$$
(30)

 n_1 and n_2 were previously determined²⁵ to be 1.590 and 1.535, respectively. Equation (30) is slightly different from the original expression in eq. (26), used by Hermans and Platzek¹⁹ and Kratky,²⁶ which can be given by

$$f_{\theta} = (1+a)f_{\Delta} - a f_{\Delta}^2 \tag{31}$$

where

$$a = \frac{2n_1^2 n_2^2}{n_v^3(n_1 + n_2)} - 1 \tag{32}$$

and where $n_v \cong n_{iso}$. The value of a constant *a* is found to be 0.63, and the angle θ is determined from

D	$A(\text{mm}^2)$	n^{\parallel}	n^{\perp}	Δn	$n_{\rm iso}$	n_v	P^{\parallel}	P^{\perp}
			τ	Jnboiled Sam	ole			
1.00	1.165	1.5315	1.5280	.0035	1.5292	1.5292	.0739	.0735
1.04	1.12	1.5320	1.5275	.0045	1.5290	1.5290	.0740	.0735
1.08	1.079	1.5323	1.5271	.0052	1.5288	1.5288	.0740	.0734
1.16	1.004	1.5327	1.5268	.0059	1.5288	1.5288	.0741	.0734
1.20	0.971	1.5331	1.5266	.0065	1.5288	1.5287	.0741	.0733
			Samr	ble Boiled for 1	15 min			
1.00	1.165	1.5318	1.5278	.0040	1.5291	1.5291	.0740	.0735
1.04	1.12	1.5322	1.5275	.0047	1.5291	1.5291	.0740	.0735
1.08	1.079	1.5325	1.5270	.0055	1.5288	1.5288	.0740	.0734
1.16	1.004	1.5328	1.5266	.0062	1.5287	1.5286	.0741	.0733
1.20	0.971	1.5331	1.5265	.0066	1.5287	1.5287	.0741	.0733
			Sam	ole Boiled for 3	30 min			
1.00	1.165	1.5321	1.5278	.0043	1.5292	1.5292	.0740	.0735
1.04	1.12	1.5325	1.5274	.0051	1.5291	1.5291	0.740	.0734
1.08	1.079	1.5332	1.5270	.0062	1.5291	1.5290	.0741	.0734
1.16	1.004	1.5336	1.5266	.0070	1.5289	1.5289	.0742	.0733
1.20	0.971	1.5338	1.5265	.0073	1.5289	1.5289	.0742	.0733
			Samr	ole Boiled for (30 min			
1.00	1.165	1.5322	1.5277	0.0045	1.5292	1.5292	.0740	.0735
1.04	1.12	1.5326	1.5273	0.0053	1.5291	1.5291	.0740	.0734
1.08	1.079	1.5332	1.5269	0.0063	1.5290	1.5290	.0741	.0734
1.16	1.004	1.5334	1.5267	0.0067	1.5289	1.5289	.0741	.0734
1.20	0.971	1.5335	1.5264	0.0071	1.5288	1.5287	.0742	.0733

Table IV Values of Cross-Sectional Area, Refractive Indices n^{\parallel} , n^{\perp} , Birefringence, Isotropic Refractive Index n_{iso} , Virtual Refractive Index n_{i} , and Polarizabilities P^{\parallel} , P^{\perp}

$$f_{\theta} = 1 - \frac{3}{2}\sin^2\theta \tag{33}$$

For a random link, the orientation function P_2 (θ) as previously calculated 27 is given by

$$P_2(\theta) = (D^2 - D^{-1})/5N_1 \tag{34}$$

where N_1 is defined as the number of random links between the network junction points (the entanglements).

Roe and Krighaum²⁸ derived an expression for the distribution function of segments at an angle θ with respect to the draw ratios.

$$\omega (\cos \theta) = \frac{1}{2} + \frac{1}{4N_1} (3 \cos^2 \theta - 1)(D^2 - D^{-1}) \quad (35)$$

Before orientation, the segments will be randomly oriented at an angle θ with respect to the draw direction. After drawing the segments will be constrained at an angle β given by

$$\tan \beta = D^{-3/2} \tan \theta \tag{36}$$

Determination of the Number of Molecules Per Unit Volume

The difference of the two main refractive indices Δn of the sample is linked with the difference in the mean polarizabilities of the macromolecule for the same directions $[\Delta P = (P^{\parallel} - P^{\perp})]$ by the relation²⁹

$$\Delta n = \frac{2\pi N}{\bar{n}} \left[\frac{(\bar{n})^2 + 2}{3} \right]^2 (P^{\parallel} - P^{\perp})$$
(37)

where N is the number of molecules per unit volume and \bar{n} is the mean refractive index of the sample



Figure 7 The relationships among n^{\parallel} and n^{\perp} and draw ratio for unboiled sample.

$$ar{n} = \left(rac{n^{\parallel} + n^{\perp}}{2}
ight)$$

To find the polarizabilities of the macromolecule in the laboratory system, we used the measured values of the refractive indices in Lorentz– Lorenz's eq. (21).

Experimental Procedure

A microstrain device was described before and used in conjunction with a two-beam polarizing interference Pluta microscope. It was modified to measure stress as well as strain^{11,12,30,31} and was used to measure both the refractive indices for the two principal vibration directions and the bire-fringence values as a function of stress, strain, and draw ratio of viscose fibers. The viscose fibers are manufactured by Misr Rayon Co. The untreated sample has T_g of 45.9°C and its crystal-linity index is 0.22.

RESULTS

The stress-strain device attached to a double refracting polarizing interference Pluta microscope was used to measure both the refractive indices for the two principal vibration directions (along n^{\parallel} and across n^{\perp}) and the birefringence Δn values as a function of stress, strain, and draw ratio of viscose fibers.

Measurement of Transverse Sectional Area

Plate 1 shows the cross section of the viscose fibers seen by high power optical microscope. According to this plate the cross-sectional view shows irregular shape. The cross-sectional area A is found to be 1.165×10^{-3} mm². The cross-sectional areas of the drawn samples are given in Table IV.

Mechanical Properties

The stress-strain device is then used with the undrawn fiber to get different draw ratios. Table I shows the obtained experimental values of different draw ratios, strain, stresses, Young's modules, strain optical coefficient C_{ε} , stress optical coefficient C_{S} , Poisson's ratio μ , the elastic shear modules G, the compressibility χ for an unboiled sample and samples boiled for 15, 30, and 60 min. The value of C_{S} is dependent on the chemical structure of the polymer, and it decreases as the draw ratio is increased.

Figure 1(a)–(d) shows the relationship between the draw ratio D and E; G, χ , and C_S for the unboiled sample; and samples boiled for 15, 30, and 60 min, respectively.



Figure 8 (a)–(d) Shows the relationships among the birefringence Δn and draw ratio for all samples.

Type of Sample	A^{\parallel}	A^{\perp}	$B^{\parallel} imes 10^2$	$B^{\perp} imes 10^2$	\mathcal{E}_{∞}
Unboiled	1.492	1.489	119	112	2.302
Boiled for 15 min	1.497	1.493	113	108	2.288
Boiled for 30 min	1.497	1.495	113	105	2.305
Boiled for 60 min	1.501	1.492	108	113	2.303

Table V Values of the Constants $A^{\parallel}, A^{\perp}, B^{\parallel}, B^{\perp}$ of Cauchy's Dispersion Equation and the Dielectric at Infinity

The relationship between stress and draw ratio is given from Mooney–Rivlin eq. (16). Figure 2 shows the relationship between $[\sigma/(D - D^{-2})]$ and D^{-1} for an unboiled sample that shows a linear relationship. The other samples showed the same behavior. The constants C_1

and C_2 were determined for the unboiled sample and samples boiled for 15, 30, and 60 min; the obtained values are given in Table II. The constant C_2 was attributed to energy dissipation resulting from chain interactions during deformation and in conformity with this view, C_2



Plate 3 (a)–(h) Some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position of the different samples at different wavelengths.



Figure 9 The relationships among $[1/(n_{iso}^2 - 1)]$ and $1/\lambda^2$.

becomes zero when the elastomer is swollen by solvents. 23

The obtained values of the above mechanical parameters given in Table I were utilized for calculating the number of network chains per unit volume N_c , the work per unit volume W, and the average work per chain W' using eqs. (12), (15), and (14), respectively. The obtained results of N_c , W, and W' are given in Table III for the unboiled sample and samples boiled for 15, 30, and 60 min, respectively. In addition, the reduction in entropy ΔS , the difference in polarizabilities along and across the axes of chain units $(b_1 - b_2)$, and the optical configuration parameter $\Delta \alpha$ were calculated from eqs. (13), (19), and (20), respectively. The obtained values of ΔS , $(b_1 - b_2)$, and $\Delta \alpha$ are given also in Table III for the unboiled sample and samples boiled for 15, 30, and 60 min, respectively. From Table III one can observe that the values of the parameter $(b_1 - b_2)$ and that of the optical configuration parameter $\Delta \alpha$ are the same. This means that the difference in polarizabilities along and across the axes of chain units $(b_1 - b_2)$ is equal to the optical configuration parameter $\Delta \alpha$.

Figure 3(a)-(d) shows the relationship between ΔS and the draw ratio, whereas Figure 4(a)-(d) shows the relationship between the number of network chains per unit volume and the draw ratio for all samples. Figure 5(a)-(d) shows the relationship between the work per unit volume and the draw ratio. Figure 6 shows the relation-

ship between the average work per chain and the draw ratio.

Double-Beam Interferometry

Viscose fiber was examined before and after applying stress by the double-beam interference microscope. Monochromatic light of wavelength $\lambda = 546$ nm for green light was used. The microscope was adjusted first to show the totally duplicated image of the examined fiber, where the two fringe shifts for light vibrating parallel and perpendicular to the fiber axis are shown. Plate 2(a)–(h) shows some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position. Plane-polarized light of $\lambda = 546$ nm was used for vibrating along and across the fiber axis, and liquid of refractive index was $n_L = 1.528$ at 21.5°C. At different

Table VI Values of Δn , $P_2(\theta)$, and the Constant $(\Delta \alpha/3\alpha_0)$

_		$(\Phi^{\parallel} - \Phi^{\perp} / \Phi^{\parallel} + 2 \Phi^{\perp})$	P_2	<i></i>
D	Δn	$ imes 10^{-4}$	(θ)	$(\Delta \alpha/3\alpha_0)$
		Unboiled Sample		
1 00	0035	18	0636	028
1.00	0045	24	0818	029
1.04	0052	2 1 97	0945	.025
1 16	0052	31	1073	020
1.10	0065	34	1189	020
1.20	.0005	04	.1102	.025
		Sample Boiled for 15	min	
1.00	.0040	21	.0727	.029
1.04	.0047	25	.0855	.029
1.08	.0055	29	.1000	.029
1.16	.0062	33	.1127	.029
1.20	.0066	35	.1200	.029
		Sample Boiled for 30	min	
1.00	.0043	23	.0782	.029
1.04	.0051	27	.0927	.029
1.08	.0062	33	.1127	.029
1.16	.0070	37	.1273	.029
1.20	.0073	38	.1327	.029
		Sample Boiled for 60	min	
1 00	0 0045	24	0818	029
1.00	0.0019	28	0964	029
1.04	0.0063	20	1145	020
1 16	0.0005	35	1918	020
1.10	0.0007	37	1901	020
1.40	0.0071	51	.1491	.049

D	f_{Δ}	$f_{ heta}$	$ heta^{\circ}$	θ'°	$f_{ heta}/f_{\Delta}$	$(f_{\theta} - f_{\Delta})/f_{\theta}$	а
			Unbo	iled Sample			
1.00	.0636	.0678	51.8	51.0	1.065	.0610	.636
1.04	.0818	.0871	51.1	50.9	1.065	.0610	.637
1.08	.0945	.1007	50.6	50.4	1.065	.0611	.637
1.16	.1073	.1142	50.1	49.8	1.065	.0610	.637
1.20	.1182	.1258	49.7	49.4	1.064	.0608	.638
			Sample B	oiled for 15 m	in		
1.00	.0727	.0774	51.5	51.3	1.065	.0609	.636
1.04	.0855	.0910	50.9	50.7	1.064	.0608	.636
1.08	.1000	.1065	50.4	50.2	1.065	.0610	.637
1.16	.1127	.1201	50.0	49.6	1.065	.0611	.638
1.20	.1200	.1278	49.6	49.3	1.065	.0609	.638
			Sample B	oiled for 30 m	in		
1.00	.0782	.0832	51.2	51.1	1.064	.0606	.636
1.04	.0927	.0987	50.7	50.5	1.064	.0606	.636
1.08	.1127	.1200	49.9	49.6	1.064	.0604	.636
1.16	.1273	.1354	49.3	49.1	1.064	.0604	.638
1.20	.1327	.1412	49.2	48.8	1.064	.0603	.637
			Sample B	oiled for 60 m	in		
1.00	.0818	.0871	51.1	50.9	1.064	.0606	.636
1.04	.0964	.1026	50.5	50.3	1.064	.0606	.636
1.08	.1145	.1219	49.8	49.6	1.064	.0604	.636
1.16	.1218	.1297	49.6	49.3	1.064	.0604	.637
1.20	.1291	.1374	49.3	49.0	1.064	.0606	.638

Table VII Values of f_{Δ} , f_{θ} , θ , θ' , the Ratio f_{θ}/f_{Δ} , and the Constant *a*

draw ratios, n^{\parallel} , n^{\perp} , and Δn were calculated for the unboiled sample and for samples boiled for 15, 30, and 60 min. The results of n^{\parallel} , n^{\perp} , and Δn are given in Table IV. Figure 7 shows the relationship between n^{\parallel} and n^{\perp} and the draw ratio for unboiled sample. The other samples showed the same behavior.

Figure 8(a)–(d) shows the relationship between Δn and draw ratio. The refractive index n^{\parallel} and the birefringence Δn increase with increasing the draw ratios, whereas the refractive index n^{\perp} decreases with increasing the draw ratios for all samples. The corresponding polarizabilities per unit volume $(P^{\parallel}, \text{ and } P^{\perp})$, the isotropic refractive index, and the virtual refractive index are calculated for all samples from eqs. (21), (23), and (24), respectively. The resultant data are given in Table IV.

The application of Cauchy's dispersion equation

$$n_{\lambda}^{\parallel} = A^{\parallel} + B^{\parallel} / \lambda^2 \tag{38}$$

with an analogous equation for n^{\perp} gives its constants A and B by plotting the relation between n^{\parallel} and n^{\perp} with $1/\lambda^2$. The constants A and B for the different samples are given in Table V. Plate 3(a)–(h) shows some of the obtained microinterferograms of two-beam interferometry from the totally duplicated image position of the different samples at different wavelengths. By plotting the relation between $[1/(n_{iso}^2 - 1)]$ and $1/\lambda^2$ (Fig. 9), the dielectric constant at infinity ε_{∞} is calculated, where $n^2 = \varepsilon_{\infty}$. The values of ε_{∞} for the different samples are given in Table V.

In addition to the above optical properties, the optical orientation function $P_2(\theta)$ is calculated from eq. (26) for all samples. The values of $(\Delta \alpha / 3\alpha_0)$ are calculated at different draw ratios for all samples and the results are given in Table VI, where it is constant for a given polymer due to its dependence on the molecular structure.

Also, the values of f_{θ} are determined due to the new approach; f_{θ} and the optical orientation angle θ (the angle between the fiber axis, the axis of the polymer units), are measured from eqs. (30) and (33), respectively, for all samples and given also in Table VII. The relationships among the draw ratio and both the optical orientation function f_{θ} and angle θ for all samples are given in Figures 10(a)-(d) and 11(a)-(d).

From the resulting values of the optical orientation function $\langle P_2(\theta) \rangle$ given by Ward and the values of angle θ , the number of random links N_1 between entanglements were calculated from eq. (34). In addition to N_1 , the distribution function of segments ω (cos θ) at an angle θ is determined with respect to the draw ratio from eq. (35). The angle β , where the segment is constrained after drawing, and the number N of molecules per unit volume were determined from eqs. (36) and (37), respectively. The values of N_1 , ω (cos θ), β , and N for all samples are given in Table VIII. The relationship between N_1 and the draw ratio is drawn in Fig. 12(a)–(d). An empirical formula is sug-



Figure 10 (a)–(d) The relationships among the optical orientation function $f(\theta)$ and draw ratio for all samples.



Figure 11 (a)–(d) The relationships among the orientation angle θ and draw ratio for all samples.

gested to evaluate the relationship between draw ratio and Δn , $f(\theta)$, W, W', A, and N_c , as follows:

$$\ln[\Delta n \ W \ W' \ f(\theta)/A \ N_c] = XD + Y \quad (39)$$

where *X* and *Y* are constants characterizing the proportionality in eq. (23). The values of *X* and *Y* were determined to be 51.25 and -167.75, respectively (see Fig. 13).

DISCUSSION

Deformation due to drawing processes is the predominant means of producing new physical structures of polymeric fibers, which are so important commercially and are of much industrial interest. Developing the properties of polymers and fibers is done by various treatments—mechanical, chemical, thermal, and others. By means of the drawing process, the development of the properties is due to change in the molecular arrangement and, hence, the creation of a new structure that tends to change polymeric properties is expected. The drawing process produces an orientation in gaining greater insight at a microstructure level when investigating mechanical properties. In addition, the thermal process may change the crystalline and amorphous parts in a rayon viscose fibers, where the crystallized areas give high modules of rigidity, elasticity, and ultimate ten-

	ω				
D	$(\cos \theta)$	$\tan \beta$	β°	N_1	N
		Unboiled	Sample		
1.00	0.500	1.234	51.0	0.000	1.000
1.04	0.519	1.156	49.1	0.295	1.000
1.08	0.526	1.075	47.1	0.520	1.000
1.16	0.533	0.946	43.4	0.904	1.000
1.20	0.540	0.886	41.5	1.032	1.000
		Sample Boile	d for 15 min		
1.00	0.500	1.248	51.3	0.000	1.000
1.04	0.522	1.148	48.9	0.283	1.000
1.08	0.529	1.066	46.8	0.492	1.000
1.16	0.536	0.950	43.6	0.861	1.000
1.20	0.541	0.880	41.5	1.016	1.000
		Sample Boile	d for 30 min		
1.00	0.500	1.239	51.1	0.000	1.000
1.04	0.525	1.140	48.7	0.260	1.000
1.08	0.536	1.045	46.3	0.436	1.000
1.16	0.545	0.923	42.7	0.762	1.000
1.20	0.550	0.868	40.9	0.920	1.000
		Sample Boile	d for 60 min		
1.00	0.500	1.230	50.9	0.000	1.000
1.04	0.527	1.132	48.5	0.251	1.000
1.08	0.537	1.045	46.3	0.429	1.000
1.16	0.542	0.939	43.2	0.796	1.000
1.20	0.547	0.874	41.2	0.945	1.000

Table VIII Values of ω (cos θ), tan β , the Angle β , the Number of Network Junction Points N_1 , and the Number of Molecules per Unit Volume N

sile strength to viscose fibers. The amorphous areas give the fibers the flexibility, recovery, elongation, and swelling. The force-extension data for the filaments could be interpreted in two ways: by a simple statistical theory owing to $Flory^{32,33}$ and via a modified Mooney–Rivlin analysis.¹⁶ The accuracy of both methods depends on how accurately the shear modulus *G* can be calculated from tensile experiment.

The measured values of the mechanical properties achieved by using the modified stressstrain device are an indication to the above facts. The measured values of Young's modules tend to decrease by drawing processes. This observation is in similar agreement with observations given by other physical processes published before.³⁴ The constant C_2 of the Mooney–Rivlin equation was attributed to energy dissipation resulting from chain interactions during deformation; in conformity with this view, C_2 becomes zero when the elastomer is swollen by solvents.¹⁶

Significant variations in the characteristic properties of viscose fibers, such as birefringence, orientation function and angle, the number of molecules per unit volume, and the distribution function of segments is due to the reorientation of molecules by drawing processes. Also, the boiling process changes the structural behavior because of accumulation of some structural phenomenon that may be summarized as follows: disorientation, recrystallization by nucleation, recrystallization by growth, shrinkage, and crystal decomposition.

CONCLUSION

From the above measurements and calculations of the various optical and mechanical parameters and their changes with the applied stresses and boiling times, the following conclusions are drawn. (1) The mechanical properties, Young's modules, elastic shear modules, and the compressibility change with applied stress as well as thermal conditions. (2) Poisson's ratios decrease with the applied stresses and are not affected by the boiling times. (3) Both stress and strain optical coefficients change with both the draw ratios and the boiling times. (4) The work per unit volume W increases with draw ratios and also changes because of boiling times. (5) The average work per chain W' increases with draw ratios but is independent of the boiling times. (6) The entropy ΔS of fibers decreases with the applied stresses and boiling times. (7) Increasing the draw ratios increased the optical configuration parameter $\Delta \alpha$. (8) As the draw ratios as well as the boiling times increase, the refractive indices n^{\parallel} and the birefringence Δn increase. (9) The electric polarizability constant is unaffected by both the draw ratios and boiling times and equals 0.029, where it depends on the molecular structure. (10) The orientation factor and orientation angle are affected by both the drawing process and boiling time. The orientation angle decreases with both, whereas the orientation factor increases. (11) The number of net-



Figure 12 (a)–(d) The relationships among the number of network junction points N_1 and draw ratio for all samples.



Figure 13 The relationships among $\ln[\Delta n \ W \ W' f(\theta)/A \ N_c)]$ and draw ratio.

work junction points N_1 increases with the drawing effect and decreases with the boiling times effect, whereas the distribution function of segments at an angle θ slightly increases with increasing the draw ratios. (12) Finally, the above experimental results and calculations confirm that the drawing and boiling of viscose fibers, in conjunction with the application of double-beam interference microscope, do change mechanical, optical, and structural parameters of these fibers.

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