Optothermal Properties of Fibers—20—Relation between Physical Structure and Mechanical Properties of Cold Drawn Polypropylene Fibers

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ABSTRACT: The structure of annealed polypropylene (PP) fibers is studied interferometrically using two-beam Pluta polarizing interference microscope connected to a device to study the draw ratio with birefringence changes dynamically. Relations of drawing changes with some optical and physical parameters are given. Evaluation of average work per chain, work per unit volume, reduction in entropy caused by elongation, and the work stored in the body as strain energy were determined. Also the resulting optical data were utilized to evaluate the orientation factor, the orientation angle, the virtual refractive index, and the number of molecules per unit volume. The value of $(\Delta \alpha/3\alpha_0)$, which depends upon the molecular structure of the polymer, remains constant. Relations between the physical and optical parameters with different strains are given for these fibers. The generalized Lorentz–Lorenz equation given by de Vries is used to determine polypropylene fiber structural parameters. Comparison between Hermans optical orientation function formula and the corrected formula by de Vries are given. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 819–831, 1999

Key words: two-beam; polypropylene; drawing; annealing; orientation; optical configuration

INTRODUCTION

It is known that optical parameters are the most sensitive indicators of the extent of anisotropy properties of polymers and, therefore, the degree of macromolecular orientation. The coefficient of birefringence is often used as a measure of polymer orientation. Structural techniques based on optical birefringence were used to measure the degree of the molecular alignment in uniaxially oriented fibers. Because most thermoplastic polymers are semicrystalline, Δn represents the overall chain orientation in crystalline and noncrystalline domains. Fibers are expected to have positive birefringence because of the better alignment and orientation of molecules along the fiber axis in both the crystalline and noncrystalline domains.¹⁻¹²

Most normally isotropic polymeric materials, because of random molecular orientation, can be made optically anisotropic by application of mechanical stress. In going from tension to compression, the material changes from positive uniaxial to negative uniaxial or vice versa, depending upon polarizability considerations. In both cases, the effective optic axis is the stress direction. The birefringence at any point is proportional to the principal stress difference. In the elastic region of the material, the birefringence can be related to the stress by $\Delta n = C_s \sigma$, where C_s is the stressoptical coefficient, which usually must be found experimentally. However, it should be remembered that the birefringence, whether because of

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stress-strain or molecular orientation, may be temperature dependent, so changes produced by elevated temperatures should be interpreted with care.

In the present work, the drawing and optical results for samples of polypropylene (PP) fibers having different annealing and cold drawing conditions (previously measured interferometrically using two-beam Pluta polarizing interference microscope connected to mechanical device) are utilized to calculate some structural parameters.¹⁴ Relationships between the calculated structural parameters are given.

THEORETICAL CONSIDERATIONS

Determination of the Number of Molecules per Unit Volume

The mean values of the refractive indices of the fiber and the total mean birefringence were calculated from the totally duplicated and nonduplicated images of the fiber using Pluta interference microscope.^{17–19}

The values of the mean polarizabilities per unit volume parallel P_a^{\parallel} and perpendicular P_a^{\perp} to the fibers axis were derived from the measured values of the refractive indices by application of Lorentz-Lorenz equations:

$$ar{P}_{_{\parallel}} = \; rac{3}{4 \, \pi} \left(rac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2}
ight)$$
 (1)

with an analogous formula for P_a^{\perp} .

These values were used in the following equation¹⁸ to calculate the number of molecules per unit volume:

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

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

$$\bar{n} = \frac{n_{\parallel} + n_{\perp}}{2}, \qquad (2a)$$

 P_{\parallel} , and \bar{P}_{\perp} are the mean polarizabilities of the macromolecules for the same direction of the mean refractive indices.

Calculation of the Virtual Refractive Index

de Vries also defined the invariant refractive index, which he calls the "virtual refractive index" n_v by the following:

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

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

$$n_{\rm iso} = \frac{\left[n_a^{\parallel} + 2n_a^{\perp}\right]}{3} \tag{4}$$

Orientation Parameters

In an approach to the continuum theory of birefringence of oriented polymer,¹⁸ it was found that

$$F_{\theta} = \left[\frac{n_1^2 n_2^2}{n_{\parallel}^2 n_{\perp}^2}\right] \cdot \left[\frac{n_{\parallel} + n_{\perp}}{n_1 + n_2}\right] \cdot \frac{\Delta n_a}{\Delta n_{\max}}$$
(5)

which is slightly different from the original simple expression for the degree of orientation used by Hermans.¹⁹

$$F_{\Delta} = \frac{\Delta n}{\Delta n_{\max}} \tag{5a}$$

Hermans's optical orientation function $F_{\Delta}[F_{\Delta} = \langle P_2(\theta) \rangle]$ has been corrected by de Vries to be F_{θ} in the range $0 < \Delta n < 0.8$ as

$$F_{\theta} = (1+a)F_{\Delta} - aF_{\Delta}^2$$

where

$$(1+a) = \frac{2n_1^2 n_2^2}{n_v^3 (n_1 + n_2)} \tag{6}$$

where n_1 , n_2 , and n_v are given from Reference 18, and $n_v \cong n_{\rm iso}$ are evaluated from eq. (3). So the constant *a* was calculated and found to be 0.5.

The optical orientation function and orientation angle can be calculated using the Hermans equations.¹⁹

$$F_{\Delta} = \frac{\Delta n}{\Delta n_{\max}} \tag{7a}$$

$$F_{\Delta} = 1 - \frac{3}{2}\sin^2\theta \tag{7b}$$

The value of $\Delta n_{\rm max}$ has been previously determined to be 0.045^{16} for perfectly (or fully) oriented fiber, and Δn_a is the measured mean birefringence.

In evaluating the orientation function for partially oriented aggregate $\langle P_2(\theta) \rangle$ is defined by Ward²⁰ in the following equation:

$$\langle P_2(\theta) \rangle = \frac{\Delta n}{\Delta n_{\max}} \tag{8}$$

which is the same function named by Hermans.¹⁹

Cunningham et al.²¹ derived a relation between the optical orientation function $\langle P_2(\theta) \rangle$ and the polarizability as follows:

$$\frac{\Phi^{\parallel} - \Phi^{\perp}}{\Phi^{\parallel} + 2\Phi^{\perp}} = \frac{\Delta\alpha}{3\alpha_0} \langle P_2(\theta) \rangle \tag{9}$$

where

$$\Phi^{\parallel} = \frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2}$$
(9a)

an analogous equation can be derived for Φ^{\perp} , and $(\Delta \alpha \backslash 3\alpha_0)$ is found to be 0.03 for polypropylene, which agrees with previous published results.²² It can be seen that the value of $[P_2(\theta)]_{opt}$ for the annealed drawn samples are shown as a function of $[DR^2 - DR^{-1}]$. The results are consistent with the deformation of a network with $N_{(1)}$ random links per chain where

$$[P_2(\theta)] = \frac{DR^2 - DR^{-1}}{5N_1} \tag{10}$$

where DR is the extension or draw ratio.

The optical orientation angle can also be found using the following equation:

$$F_{\theta} = 1 - \frac{3}{2}\sin^2\theta \tag{11}$$

where θ is the angle between the axis of polymer unit and the fiber axis.

Roe and Krigbaum²² derived an expression for the distribution of segments at an angle θ with respect to the draw ratio.

$$\omega(\cos \theta) = \frac{1}{2} + \frac{1}{4N_c} (3 \cos^2 \theta - 1) [DR^2 - DR^{-1}]$$
(12)

From eq. (12), we found the distribution of segments varies from 0.50 to 0.66.

Before orientation, the segments are randomly oriented at an angle θ with respect to the draw direction. After a draw ratio DR, the segments are constrained at an angle β given by

$$\tan \beta = DR^{-3/2} \tan \theta \tag{13}$$

Number of Chains per Unit Volume

The Kuhen–Treloar-type theory gives²³

$$F_{(\theta)} = \frac{2}{5} N_c [DR^2 - DR^{-1}]$$
(14)

where N_c is the number of chains per unit volume and depends upon the number of crystallites in the polymer material, and $DR = l/l_0$, and DR = $1 + \varepsilon$.

The average work per chain W' could be given by the following equation²⁴:

$$W' = \frac{3KT}{2} \left| \frac{1}{3} \left(DR^2 - DR^{-1} \right) + \left(DR^{-1} - 1 \right) \right|$$
(15)

where K = Boltzman's constant, and T = absolute temperature.

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

$$W = \frac{vKT}{2} \left[(DR^2 - DR^{-1}) + 3(DR^{-1} - 1) \right]$$
(16)

Because the stress is related to the elongation, the work per unit volume is given by

$$\sigma = \frac{\partial W}{\partial DR} = vKT[DR - DR^{-2}] \qquad (17)$$

For an ideal network²⁴

$$v = \frac{N_{\rm Av}}{\rm M_c}\rho \tag{17a}$$

			Ę	a. Unanneale	d			
Draw Ratio	n_a^{\parallel}	n_a^{\perp}	$n_{\rm iso}$	n_v	θ	N_1	N	N_C
1	1 502	1 499	1 500	1 500	52.07	_	1 001	
2	1.502	1.400	1.500	1.500	36.47	1 500	1.001	0.370
3	1.525	1.504	1.511	1.511	35.67	3545	1.005	0.576
4	1.526	1.503	1.510	1 510	34 86	6 163	1.005	0.100
5	1.520 1.527	1.503	1.511	1 510	34 04	9,300	1.005	0.059
6	1.529	1.503	1.511	1.511	31.95	12.40	1.006	0.035
			b. 4	Annealed at 7	0°C			
1	1,505	1,499	1.501	1.501	48.44		1.001	
3	1.509	1.487	1.494	1.494	35.67	3,545	1.005	1.446
4	1.511	1.488	1.495	1.495	34.86	6.163	1.005	0.158
5	1.511	1.487	1.495	1.494	34.04	9.299	1.005	0.091
6	1.512	1.487	1.495	1.495	32.79	12.90	1.006	0.043
			c. A	nnealed at 10)0°C			
1	1.486	1.493	1.490	1.490	61.57	_	0.998	_
3	1.510	1.491	1.497	1.497	38.45	4.105	1.004	0.136
4	1.511	1.491	1.497	1.497	37.66	7.087	1.004	0.079
5	1.512	1.491	1.498	1.498	36.47	10.63	1.005	0.052
6	1.513	1.490	1.497	1.497	34.86	14.02	1.005	0.040
7	1.513	1.490	1.497	1.497	34.86	19.12	1.005	0.029
			d. A	Annealed at 13	30°C			
1	1.484	1.498	1.493	1.493	71.56		0.997	
2	1.514	1.501	1.505	1.505	43.47	2.423	1.003	0.230
3	1.515	1.501	1.505	1.505	42.70	5.571	1.003	0.100

 Table I
 Values of Refractive Indices, Orientation Angle, Number of Random Links/Chain, Number of Molecules/Unit Volume, and Number of Chains/Unit Volume

where ρ , polymer density for PP, was 0.869 gm/ cm³; $N_{\rm Av}$ is Avogadro's number; M_c is the average molecular weight of chain segments in the network equal to 42.08 for PP fibers.

The resulting eq. (17), relating the stress and strain, can be given by

$$\sigma = G[DR - DR^{-2}] \tag{18}$$

where *G* is the elastic shear modulus, G = vKT, an especially important relationship when the Poisson's ratio ≈ 0.5 and *G* is given by

$$G = E/3 = vKT \tag{19}$$

where E is Young's modulus.

In addition, the elongation leads to a reduction in the entropy ΔS by the following equation.²⁵

$$\Delta S = -\frac{1}{2} K v \left| (1+\varepsilon)^2 + \frac{2}{(1+\varepsilon)} - 3 \right| \quad (20)$$

The greatest difficulties in applying Equations from (16) to (20) arise in assigning a suitable value to v and establishing the conditions to achieve equilibrium relaxation. In the present work we do not discuss these difficulties. Also, we consider ($v = 12.432 \times 10^{21}$) because there are difficulties in evaluating the densities for different draw ratios.

Mooney–Rivlin Equation

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

a. Unannealed							
Draw	$E imes10^8$	$\sigma imes 10^7$	$C_{ m s} imes 10^{-10}$	$\Delta a imes 10^{-24}$			
Ratio	(Pa)	(Pa)	cm ³ /dyne	cm ³			
1		_	_	_			
2	9.11	9.11	2.30	0.244			
3	7.52	15.04	1.46	0.155			
4	6.84	20.52	1.11	0.118			
5	6.45	25.82	0.93	0.098			
6	6.22	31.09	0.83	0.088			
		b. Annealed a	at 70°C				
1	_	_	_	_			
3	7.52	15.04	1.46	0.155			
4	6.84	20.52	1.12	0.118			
5	6.45	25.82	0.93	0.098			
6	6.22	31.09	0.80	0.088			
		c. Annealed a	t 100°C				
1							
3	7.52	15.04	1.26	0.155			
4	6.84	20.52	0.97	0.118			
5	6.45	25.82	0.81	0.098			
6	6.22	31.09	0.74	0.088			
7	6.22	31.09	0.63	0.088			
		d. Annealed a	t 130°C				
1							
2	9.11	9.11	1.42	0.151			
3	7.52	15.04	0.93	0.098			

Table IIValues of Young's Modulus, Stress, Stress Optical Coefficient, andOptical Configuration Parameters

$$W'' = C_1 [DR^2 + 2DR^{-1} - 3] + C_2 [DR^{-2} + 2DR^{-3}]$$
(21)

and

$$\sigma = \frac{W''}{\partial DR} = C_1 [2DR - 2DR^{-2}] + C_2 [2 - 2DR^{-3}] \quad (22)$$

or

$$\sigma = 2[C_1 + C_2 D R^{-1}][DR - DR^{-2}] \qquad (23)$$

Eq. (23) is the well-known Mooney–Rivlin equation. A plot of the reduced stress $\sigma/2(DR - DR^{-2})$ as a function of reciprocal elongation DR^{-1} gives a straight line whose slope is C_2 and

whose intercept with the ordinate is C_1 . In practice, the constant C_1 has proved to be a useful measure of the crosslink density.²⁵

Thus, similarly, the birefringence strain relation was given by the following equation.

$$\Delta n = [DR - DR^{-2}][A_1 + A_2 DR^{-1}] \qquad (24)$$

A plot of

$$\frac{\Delta n}{[DR - DR^{-2}]} \tag{24a}$$

as a function of reciprocal elongation DR^{-1} gives a straight line whose slope is A_2 and whose intercept with the ordinate is A_1 .

In general, the ratio C_2/C_1 approximately equals A_2/A_1 , so that the birefringence remains proportional to the stress. If the rubber is swollen with a



Plate 1a–c and Plate 2a–c Some obtained microinterferograms of two-beam interferometry from the totally duplicated image of PP fiber at different draw ratios of (λ = 546 N M).

solvent, the ratio C_2/C_1 decreases and eventually becomes zero for high enough degrees of swelling.

Stress Optical Coefficient

For the uniaxial tensile stress, the birefringence and the retractive stress are related by eq. (25). The value of C_s is dependent upon the chemical structure of the polymer. Moreover, the value of this coefficient depends solely upon the mean refractive index and the optical anisotropy of the random link, as seen on the following equation.

$$\frac{\Delta n}{\sigma} = C_s = \frac{2\pi}{45KT} - \frac{(\bar{n}^2 + 2)^2}{\bar{n}} [\alpha_{\parallel} - \alpha_{\perp}] \quad (25)$$

where n is the average refractive index, and α^{\parallel} and α^{\perp} are the polarizabilities along and across the axis of such units. K is Boltzman's constant, and T is the absolute temperature. In addition, C_s is independent of the chain length and the degree of crosslinking. From the above equation, it can be seen that birefringence in elastomers is proportional to the applied stress.

Calculation of the Optical Configuration Parameter⁸

The optical configuration parameter Δa is related to the stress–optical coefficient C_s by the following equation.

$$\Delta a = \frac{(45KTC_s/2\pi)\bar{n}}{(\bar{n}^2 + 2)^2}$$
(26)

where K and T are as described above. Values of Δa at different values of \bar{n} and C_s are summarized in Table II.

EXPERIMENTAL

Samples Preparation

Annealing Process

The PP fibers were wound in a cocoon form on glass rods with free ends. They were then annealed in an electric oven, where the temperature was adjusted to 70, 100, and $130 \pm 1^{\circ}$ C with constant annealing times 4 h, then left to cool in air at 28 ± 1°C.

Application of Two-Beam Interferometry

The totally duplicated image of the fiber obtained with Pluta polarizing interference microscope, discussed in detail elsewhere,^{15–17} was used to calculate the mean refractive indices n_a^{\parallel} and n_a^{\perp} of PP fibers.

RESULTS

Plate 1(a-d) and Plate 2(a-d) are microinterferograms of the totally duplicated images for annealed PP fibers using the Pluta microscope with different draw ratios before and after annealing temperatures. The refractive index of the immersion liquid was selected to allow the fringe shift to be small and corrected according to the variation of the wavelength. Plates 1 and 2 also show that the fringes shift changed as the annealing temperature and wavelength increased. Using these microinterferograms, the mean refractive index in the parallel and perpendicular directions at different annealing temperatures and constant annealing time were calculated.

Figure 1a-d shows the relation between the birefringence Δn and the refractive indices differences $(n^{\parallel} - n_v, n^{\perp} - n_v, n^{\parallel} - n_{\rm iso})$, and $n^{\perp} - n_{\rm iso}$). From Figure 1, n_v and $\Delta n_{\rm max}$ are used to predict the values of the refractive indices n_1 and n_2 for fully oriented fibers. These values are found to be 1.552 and 1.507, respectively, at 28 ± 1°C.

Table I gives some experimental results for the refractive indices, and the following calculated values, virtual refractive index (n_v) , and isotropic refractive index, which were calculated by using eq. (4) for annealing PP fibers.

 F_0/F_{Δ} could be found for drawing PP fibers and quenched in air. These results give $(F_{\theta} - F_{\Delta})/F_{\theta}$, which are in fair agreement with similar polymers (PP, PE, nylon 6, and cellulose) by de Vries,¹⁸ with a deviation under 3%.

Figure 2 shows the relation between corrected values of optical orientation function F_{θ} and the Hermans function F_{Δ} for annealing polypropylene fibers. The calculated values of the orientation angle θ from F_{θ} , the number of molecules per unit volume N, the number of random links per chain N_1 , and the number of network chain per unit volume N_c at different draw ratios are given in Table Ia–d.

Table II give the calculated values of moduli of elasticity in tension E, the values of stress σ , the stress optical coefficient C_s , and the optical configuration parameters Δa .

Figure 3 shows the relation between the birefringence Δn and the optical orientation function F_{θ} for different draw ratios. Figure 4 shows the relation between $\langle P_2(\theta) \rangle$ and $[DR^2 - DR^{-1}]$, which is a straight line. From it, we calculated the values of random links per chain N_1 . Figure 5 shows the variation of orientation angle θ , calculated from eq. (12), of PP fiber with different draw ratios before and after annealing at 70, 100, and 130 \pm 1°C, respectively, (at constant annealing time 4 h). It shows that orientation angle is decreased by increasing the draw ratio. Figure 6a–b



Figure 1a–d Relation between the birefringence Δn and the refractive indices differences $n^{\parallel} - n_{\rm iso}$ and $n^{\perp} - n_{\rm iso}$) of PP fiber before and after annealing at 70, 100, and 130°C with different draw ratios.

shows the relation between tan β and draw ratios at different annealing temperatures and constant annealing time 4 h, using θ ; tan β decreases with increasing the draw ratio. Figure 7 shows the variation of $(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})$ of PP fibers because of changing of draw ratios before and after annealing (at constant times 4 h). Figure 8 shows the variation of $(\Phi^{\parallel} - \Phi^{\perp})/\Phi^{\parallel} + 2\Phi^{\perp}$ with changing $P_2(\theta)$ caused by changing of draw ratios before and after annealing (at constant times 4 h). Figure 9 shows the relationship between the work per unit volume W and the draw ratios. Figure 10

shows the relationship between the work per chain W' and the draw ratios. Figure 11 shows the relationship between the strain energy W'' and the draw ratios. Figure 12 shows the relationship between the entropy ΔS and the draw ratios. Figure 13 shows the relationship between the birefringence Δn_a and the entropy ΔS at different annealing conditions and different draw ratios. Figure 14 shows the relationship between the birefringence Δn_a and the work per unit volume W at different annealing conditions and the draw ratios. Figure 14 shows the relationship between the birefringence Δn_a and the work per unit volume W at different annealing conditions and the different draw ratios.



Figure 2 Relation between corrected values of optical orientation function F_{θ} and the Hermans function F_{Δ} of PP fiber before and after annealing at 70, 100, and 130°C with different draw ratios.

DISCUSSION

The optomechanical annealed polymer characterizes several changes caused by variations in the cohesive forces between adjacent molecules. Therefore, upon drawing and annealing conditions, fol-



Figure 4 Relation between $\langle P_2(\theta) \rangle$ and $[DR^2 - DR^{-1}]$ of PP fiber before and after annealing at 70, 100, and 130°C with different draw ratios.

lowing the obtained optical and mechanical parameters results, we obtained a polymeric material with modified physical properties that, can aid in the main end use. Moreover, the present work greatly strengthens the idea that the application of twobeam interferometery, in conjunction with a me-



Figure 3 Relation between birefringence Δn_a and optical orientation function F_{θ} of PP fiber before and after annealing at 70, 100, and 130°C with different draw ratios.



Figure 5 Relation between orientation angle (θ) and different draw ratios for PP fiber before and after annealing at 70, 100, and 130°C with different draw ratios.



Figure 6 Relation between tan β and different draw ratios for PP fiber before and after annealing at 70, 100, and 110°C with different draw ratios, using θ .

chanical device, is suitable for determining optomechanical properties. Knowledge of these mechanical variations with optical parameters is valuable for characterizing the optomechanical properties of thermally treated fibers using our technique.

When a bulk polymer is crystallized in the absence of external forces, there is no preferred orientation of crystallites or molecules. If a specimen



Figure 8 Variation of $(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})$ with changing $P_2(\theta)$ attributable to changing of draw ratios before and after annealing at 70, 100, and 130°C.

is subjected to such an external force, as mechanical drawing, the crystallites and molecules become oriented. The polymer is stronger in the draw direction than in any other direction and is weakest in directions 90° to the draw direction. The increase in strength in the draw direction may be as much as 25-fold. Moreover, a change in temperature will affect the behavior of polymeric



Figure 7 Relation between $(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})$ and draw ratios for PP fibers before and after annealing at 70, 100, and 130°C.



Figure 9 Relation between the work per unit volume *W* and the draw ratios of PP fiber.



Figure 10 Relation between the average work per chain *W*' and the draw ratios of PP fiber.

material. Yield characteristics of polymeric materials are affected by changes with different annealing conditions (time and temperature).

From Figures 9–11, it is found that, in contrast to the increase of W', the work W and storable energy of the network W'' are found to decrease with increasing the draw ratios. The relationship between stress and draw ratios is given from Mooney–Rivlin eq. 23. The constants C_1 and C_2 are determined for unannealed and annealed samples, and the obtained values are given in Table III. The constant C_2 has been attributed to energy dissipation resulting from chain interac-



Figure 11 Relation between the strain energy W'' and the draw ratios of PP fiber.



Figure 12 Relation between birefringence ΔS and the draw ratios of PP fiber.

tions during deformation. Moreover, A_1/A_2 , approximately equals the ratio C_1/C_2 , which indicates that the birefringence remains proportional to the stress. The reduction in entropy ΔS (Fig. 12) with increasing the draw ratios and the same behavior with Δn (Fig. 13) clarify creation of new physical structure attributable to kinetic degradation, which tends to changes polymeric properties.

In the present study, it is clear that the optical properties of PP fibers change under the effect of annealing and cold drawing actions.



Figure 13 Relation between birefringence Δn and the entropy ΔS , of PP fiber with different draw ratios.

Sample	$C_1 imes 10^7$	$C_{2} imes 10^{7}$	C_{2}/C_{1}	A_1	$A_2 imes 10^{-5}$	A_2 / A_1
Unannealed	2.5917	0.06131	0.0236	0.0243	9.00	0.003
70	2.5917	0.06131	0.0236	0.0243	9.00	0.003
100	2.5917	0.06131	0.0236	0.0204	26.6	0.013

Table III Values of the Constants C_1 , C_2 , A_1 , and A_2

When PP is deformed by annealing and drawing, the individual crystalline particles slide past each other to take up new positions, where they are held together just as strongly as in the original material because of the formation of fresh, interatomic bonds. Thus, the molecules pass from an unoriented state to an oriented state. Studying the continuous mechanical and optical changes occurring gives information about the decrease in entropy and increase in orientation. In addition when optical properties are considered, crystallinity is invariably important, because the crystalline component is always of a higher refractive index than the amorphous regions.

CONCLUSIONS

It is clear that two-beam Pluta polarizing interference microscope in conjunction with the me-



Figure 14 Relation between birefringence Δn_a and the work per unit volume *W* of PP fiber with different draw ratios.

chanical device is a useful and rapid technique to clarify the optical and mechanical parameters of PP fibers with different annealing and drawing conditions. Because of the measurements of the changes in optical and mechanical parameters to the thermal effects in PP fibers, the following conclusions may be drawn.

- 1. It is clear that there are isothermal kinetic changes attributable to the drawing process confirmed from changes of ΔS (Fig. 12).
- 2. The orientation angle decreases with increasing draw ratio; whereas, the orientation factor increases.
- 3. The results shown in Table IIa-d indicate that the stress optical coefficient varies with different draw ratios at different annealing conditions.
- 4. It is clear that there are changes in the calculated values of the isotropic refractive indices attributable to the application of different formulae. In comparison, it is found that $n_v \approx n_{\rm iso}$.
- 5. Study of the rate of change with respect to the draw ratio reveals that the mechanical properties of the structure in a direction perpendicular to the fiber axis differ from those in an axial direction, which is expected for an anisotropic properties.
- 6. A change of ΔS because of the drawing process can change the optical property Δn of PP fibers. In addition, the retractive forces of the network are produced by the decrease in entropy of freely jointed chains when stretched.
- 7. Various mechanical structural parameters of the drawn samples are determined in a simple way by calculations dependent on stress-strain phenomena. These mechanical parameters throw light on such physical phenomena as swelling and thermal, and optical effects.

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