Interferometric determination of (skin-core) optical and orientation structural parameters of

drawn polypropylene fibres

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M A Kabeel[1]

Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract
Multiple-beam Fizeau fringes in transmission were used to study the changes of the principal optical properties of six samples of drawn polypropylene fibres. The resulting data of the mean, skin and core refractive indices and birefringence of these fibres were used to calculate some structural parameters such as the optical orientation function, orientation angle, the isotropic refractive index, the virtual refractive index, the number of molecules per unit volume and the random links per chain. Poisson's ratio and the strain optical coefficient are also determined. The distribution of segments at an angle with respect to the draw ratio and the electric polarizability constant ($\Delta\alpha/3\alpha_0$) and other parameters and constants are determined. The generalized Lorentz–Lorenz equation given by de Vries has been used to compare the results obtained by Herman's optical orientation function. Microinterferograms, tables and graphs are given for illustration.

1. Introduction

Measurement of optical anisotropy or birefringence provides structural information about the orientation of a particular molecular system. The values of retractive indices and birefringence for each layer of the fibre give useful information for the characterization of the fibre on the molecular level. Microinterferometry is a useful technique for the determination of these optical properties. A detailed survey of the investigations, methods and techniques of microinterferometry applied to fibrous materials has been given [1]. Both two-beam and multiple-beam microinterferometric techniques were used to study the optical properties of polypropylene fibres [2–4]. Recently, extensive applications were used to evaluate the effect of mechanical, thermal, or chemical treatments of natural and man-made fibres [5–7].

In this work the optical parameter results for six samples of polypropylene (PP) fibres having different draw ratios are utilized to calculate some structural parameters. Relationships are given between optical structural parameters.

[1] Present address: Physics Department, College of Science, King Saud University, Al-Gasseem Branch, Buriedah, Kingdom of Saudi Arabia.

2. Theoretical consideration

The mean refractive indices of a fibre for light vibrating parallel and perpendicular to its axis ($n_a^\parallel$ and $n_a^\perp$), the skin refractive indices ($n_s^\parallel$ and $n_s^\perp$) and the core refractive indices ($n_c^\parallel$ and $n_c^\perp$) were determined from the microinterferograms of multiple-beam Fizeau fringes [3]. The mean birefringence Δn_a, skin birefringence Δn_s and core birefringence Δn_c of the fibre were calculated.

The polarizabilities per unit volume parallel $P^\parallel$ and perpendicular $P^\perp$ to the fibre axis were derived from the measured values of the refractive index by application of the Lorentz–Lorenz equations [8]:

$$P^\parallel = \frac{3}{4\pi}\left[\frac{n_\parallel^2 - 1}{n_\parallel^2 + 2}\right] \tag{1}$$

with a similar equation in the perpendicular direction

$$P_{iso} = \left[\frac{P^\parallel + P^\perp}{3}\right] \tag{2}$$

and P_{iso} the isotropic polarizability.

The following equation [9] was used to calculate the number of molecules per unit volume N:

$$N = \frac{\Delta n \bar{n}}{2\pi}\left[\frac{3}{\bar{n}^2 + 2}\right]^2\left[\frac{1}{P^\parallel - P^\perp}\right] \tag{3}$$

where $\bar{n}$ is the mean refractive index of the sample, which considered $\bar{n} = [(n^\parallel + n^\perp)/2]$, $[P^\parallel - P^\perp]$ equals the mean polarizabilities of the macromolecules for the same direction of the mean refractive indices and Δn is the mean birefringence.

de Vries [10] gave a theory on the basis of an internal field with the aid of the classical electromagnetic theory, in which he generalized the Lorentz–Lorenz equation. He defined also a virtual value of refractive index n_v which replaces the refractive index of isotropic material n_{iso}.

$$n_v = \sqrt{1 + \frac{3[n_\parallel^2 - 1][n_\perp^2 - 1]}{[n_\perp^2 - 1] + 2[n_\parallel^2 - 1]}} \tag{4}$$

given by

$$n_{iso} = \frac{n^\parallel + 2n^\perp}{3}. \tag{5}$$

Birefringence is a measure of the total molecular orientation of a system. The optical orientation function was defined by Hermans [11] as

$$F_\Delta = \frac{\Delta n_a}{\Delta n_{max}} \tag{6}$$

where Δn_a is the value of the measured mean birefringence and Δn_{max} is the maximum birefringence for a fully oriented fibre. F_Δ values range between $(1, 0, -0.5)$ according to the state of orientation, perfect, random or perpendicular to the fibre axis, respectively. The value of Δn_{max} has been previously determined to be 0.045 [10] for polypropylene fibres.

The optical orientation angle can be calculated using the following equation [11]:

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

where θ is the angle between the axis of the polymer units and the fibre axis. The average value of the optical orientation function for partially orientated aggregate $\langle P_2(\theta) \rangle$, due to Ward [12], is given by

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

which is the same function as named by Hermans [11].

Cunningham *et al* [13] derived a relation between the optical orientation function $\langle P_2(\theta) \rangle$ and the polarizability per unit volume as follows:

$$\left[\frac{\Phi^{\parallel} - \Phi^{\perp}}{\Phi^{\parallel} + 2\Phi^{\perp}} \right] = P_2(\theta_m) \langle P_2(\theta) \rangle \tag{9}$$

where $\Phi^{\parallel}$ and $\Phi^{\perp}$ are the polarizabilities parallel and perpendicular to the fibre axis, and $P_2(\theta_m) = \frac{1}{2}(3 \cos^2 \theta_m - 1)$ is a constant dependent only on the molecular structure of the polymer and determined by angle θ_m, the angle between the dipole moment and the chain axis. Also, equation (9) can be written in the form

$$\left[\frac{\Phi^{\parallel} - \Phi^{\perp}}{\Phi^{\parallel} + 2\Phi^{\perp}} \right] = \left(\frac{\Delta \alpha}{3\alpha_0} \right) \langle P_2(\theta) \rangle \tag{10}$$

where $\Delta \alpha$ is the difference between $\alpha^{\parallel}$ and $\alpha^{\perp}$, which are the electric polarizability of one molecule when using monochromatic light vibrating parallel and perpendicular to the fibre axis, respectively, and $\alpha_0 = (\alpha^{\parallel} + 2\alpha^{\perp})/3$ is the isotropic polarizability. The quantity $(\Delta \alpha / 3\alpha_0)$ depends on the molecular structure, and is nearly constant for a given polymer [14], and the values of $\Phi^{\parallel}$ and $\Phi^{\perp}$ can be determined from the Lorentz–Lorenz equation

$$\Phi^{\parallel} = \frac{4}{3}\pi N \alpha^{\parallel} = \frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2}$$

$$\Phi^{\perp} = \frac{4}{3}\pi N \alpha^{\perp} = \frac{n_{\perp}^2 - 1}{n_{\perp}^2 + 2} \tag{11}$$

where N is the number of molecules per unit volume.

The values of $P_2(\theta)$ for the drawn samples are related to the extension or draw ratio, DR, according to the following equation [15]:

$$P_2(\theta) = \frac{DR^2 - DR^{-1}}{5N_c} \tag{12}$$

where N_c is the number of random links between the network junction, and $DR = l/l_0$, l_0 is the initial length of the fibre and l is its length after drawing.

Roe and Krigbaum [16] used an expression for the distribution of segments at an angle θ with respect to the draw ratio DR,

$$\omega(\cos \theta) = \frac{1}{2} + \frac{1}{4N_c}(3 \cos^2 \theta - 1)\left(DR^2 - \frac{1}{DR} \right). \tag{13}$$

Before orientation, the segments will be randomly oriented at an angle θ with respect to the draw direction. After a draw ratio DR then the segments will be constrained at an angle β given by [16]

$$\tan \beta = DR^{-3/2} \tan \theta. \tag{14}$$

The optical orientation function F_θ was given by the continuum theory of birefringence of an oriented polymer [10] as

$$F_\theta = \left(\frac{n_1^2 n_2^2}{n_{\parallel}^2 n_{\perp}^2} \right) \left(\frac{n^{\parallel} + n^{\perp}}{n_1 + n_2} \right) \frac{\Delta n_a}{\Delta n_{max}} \tag{15}$$
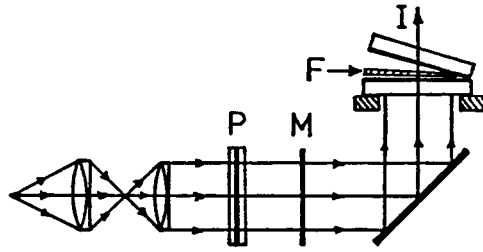
Figure 1. The setup for producing multiple-beam Fizeau fringes in transmission. P, polarizer; M, monochromatic filter; F, fibre immersed in silvered liquid wedge interferometer; I, camera attached to a microscope.
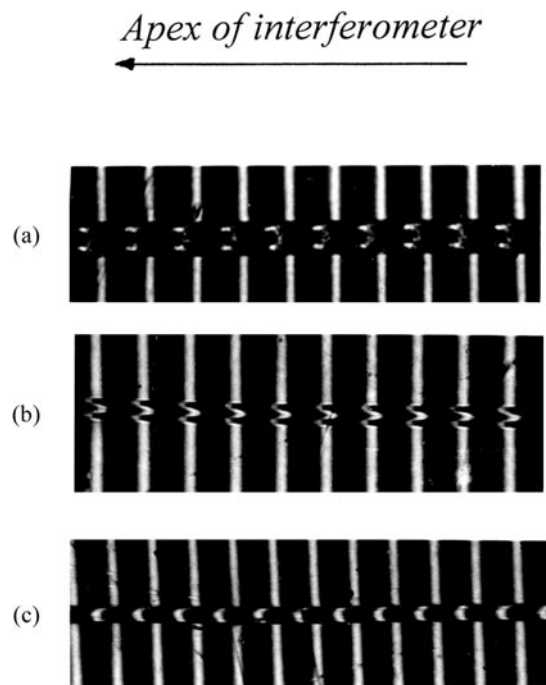

Figure 2. Microinterferograms of multiple-beam Fizeau fringes in transmission for polypropylene fibres with different draw ratios, (a) 1.0, (b) 3.0 and (c) 3.5, using light of wavelength 546.1 nm vibrating parallel to the fibre axis.

where n_1 and n_2 are the refractive indices of a fully oriented fibre, when using monochromatic light vibrating parallel and perpendicular to the fibre axis. Equation (15) is slightly different from the original equation (6) used by Hermans [11] and Kratky and Platzek [17], as follows:

$$F_\theta = (1+a)F_\Delta - aF_\Delta^2 \tag{16}$$

where

$$(1+a) = \frac{2n_1^2 n_2^2}{n_v^2 (n_1 + n_2)} \tag{17}$$

n_1, n_2 are given from [10] as 1.521 and 1.476, respectively, and n_v was calculated. So, the constant a was calculated and found to be 0.99 for polypropylene.

Table 1. Refractive indices $n_a^{\parallel}$, $n_s^{\parallel}$, $n_c^{\parallel}$, $n_a^{\perp}$, $n_s^{\perp}$, $n_c^{\perp}$ and birefringences Δn_a, Δn_s, Δn_c for the set of polypropylene fibres. The error in $n^{\parallel}$ and $n^{\perp}$ is ± 0.0007.

Draw ratio	Light vibrating parallel to the fibre axis			Light vibrating perpendicular to the fibre axis			Mean birefringence Δn_a	Skin birefringence Δn_s	Core birefringence Δn_c
	$n_a^{\parallel}$	$n_s^{\parallel}$	$n_c^{\parallel}$	$n_a^{\perp}$	$n_s^{\perp}$	$n_c^{\perp}$			
1	1.5028	1.5032	1.5015	1.5001	1.5007	1.4998	0.0027	0.0025	0.0017
3	1.5205	1.5210	1.5191	1.4993	1.5002	1.4968	0.0212	0.0208	0.0223
3.5	1.5228	1.5230	1.5222	1.4976	1.4984	1.4952	0.0252	0.0246	0.0270
4	1.5241	1.5242	1.5238	1.4956	1.4970	1.4954	0.0276	0.0272	0.0284
4.5	1.5249	1.5249	1.5250	1.4961	1.4865	1.4950	0.0288	0.0284	0.0300
5.2	1.5258	1.5256	1.5261	1.4961	1.4965	1.4954	0.0296	0.0291	0.0307

As we applied the multiple-beam Fizeau fringes in transmission, we can obtain all the previous mentioned structural parameters for the skin and core layers of the fibres.

3. Experimental results

Figure 1 shows the optical system used to produce multiple-beam Fizeau fringes in transmission. A parallel beam of plane polarized monochromatic light of wavelength λ is used to illuminate a wedge interferometer placed on a microscope stage. The fibre is immersed in a liquid and its orientation is perpendicular to the edge of wedge. Straight line fringes parallel to the edge of the wedge are formed in the liquid region. The amount, shape and direction of fringe shift crossing the fibre depends on the refractive index of liquid n_L, the relative refractive indices of the skin and core and on the wavelength and the state of polarization of monochromatic light used. Mathematical expressions were derived by Hamza and Kabeel [2] for the shape of multiple-beam Fizeau fringes crossing multilayer fibres of regular transverse sections immersed in a silvered liquid wedge.

Figures 2(a)–(c) are microinterferograms of multiple-beam Fizeau fringes in transmission for polypropylene fibres with different draw ratios 1.0, 3.0 and 3.5, respectively. Monochromatic light of wavelength 546.1 nm vibrating parallel to the fibre axis was used. The immersion liquid in these figures was selected to allow the fringe shift to be small and to determine accurately the point of connection of the fringe in the liquid. At 22 °C the refractive index of the immersion liquid was $n_L = 1.5015$ for microinterferogram 2(a), whilst for the other microinterferograms $n_L = 1.5192$. The fringe shifts in the fibre were found to be toward the apex of the interferometer. This means that the refractive indices of the chosen liquids were smaller than those of the fibres.

Figures 3(a)–(c) are microinterferograms of multiple-beam Fizeau fringes in transmission for polypropylene fibres with different draw ratios 1.0, 3.0 and 3.5, respectively. Monochromatic light of wavelength 546.1 nm vibrating perpendicular to the fibre axis was used and n_L was 1.5015 at 22.5 °C. The fringe shifts were found to be away from the apex of the interferometer for all fibres with different draw ratios. The microinterferograms of polypropylene fibres show that fibres have skin–core structure and the fringes shift changed as the draw ratio increased. Using these interferograms the refractive indices n_a, n_s and n_c and birefringence Δn_a, Δn_s and Δn_c were measured with the method described by Hamza and Kabeel [3], and the results are given in table 1.

Results show that the refractive index of the fibre $n^{\parallel}$ and its birefringence Δn continued
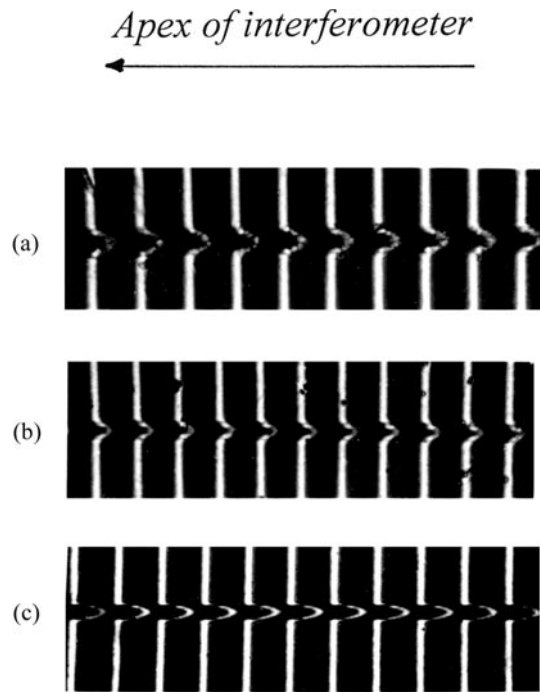
Apex of interferometer

$\longleftarrow$

Figure 3. Microinterferograms of multiple-beam Fizeau fringes in transmission for polypropylene fibres with different draw ratios, (a) 1.0, (b) 3.0 and (c) 3.5, using light of wavelength 546.1 nm vibrating perpendicular to the fibre axis.

Table 2. Isotropic indices $n_{iso(a)}$, $n_{iso(s)}$, $n_{iso(c)}$, virtual refractive indices $n_{v(a)}$, $n_{v(s)}$, $n_{v(c)}$ and isotropic polarizability $P_{iso(a)}$, $P_{iso(s)}$, $P_{iso(c)}$.

Draw ratio	$n_{iso(a)}$	$n_{iso(s)}$	$n_{iso(c)}$	$n_{v(a)}$	$n_{v(s)}$	$n_{v(c)}$	$P_{iso(a)}$	$P_{iso(s)}$	$P_{iso(c)}$
1	1.5010	1.5003	1.5015	1.5010	1.5003	1.5015	0.0703	0.0702	0.0704
3	1.5064	1.5042	1.5071	1.5062	1.5040	1.5069	0.0709	0.0707	0.0710
3.5	1.5060	1.5042	1.5066	1.5057	1.5039	1.5063	0.0709	0.0707	0.0701
4	1.5057	1.5049	1.5061	1.5054	1.5045	1.5057	0.0708	0.0707	0.0709
4.5	1.5057	1.5050	1.5051	1.5053	1.5046	1.5056	0.0708	0.0708	0.0709
5.2	1.5060	1.5056	1.5062	1.5056	1.5052	1.5058	0.0709	0.0708	0.0709

to increase with the draw ratio. This behaviour means that the polymer molecules will tend to be aligned parallel to the fibre axis as the fibre is subjected to an extension during drawing processes. Also, $n_c^{\parallel}$ takes lower values than $n_s^{\parallel}$, but by increasing the draw ratio $n_c^{\parallel}$ will reach $n_s^{\parallel}$.

The calculated values of isotropic refractive index n_{iso}, virtual refractive index n_v, and isotropic polarizability P_{iso} with respect to draw ratio and for the mean, skin and core refractive indices of polypropylene fibres are given in table 2.

Figures 4(a)–(c) show the relations between the birefringence Δn and the refractive indices differences ($n^{\parallel} - n_v$, $n^{\perp} - n_v$, $n^{\parallel} - n_{iso}$ and $n^{\perp} - n_{iso}$) at different draw ratios, for mean, skin and core values. Figure 4, n_v and $\Delta n_{\max}$ were used to predict the values of refractive indices n_1 and n_2 for fully oriented fibres. These values are found to be 1.521 and 1.476, respectively at 22.5 °C, which are in agreement with published values [17].

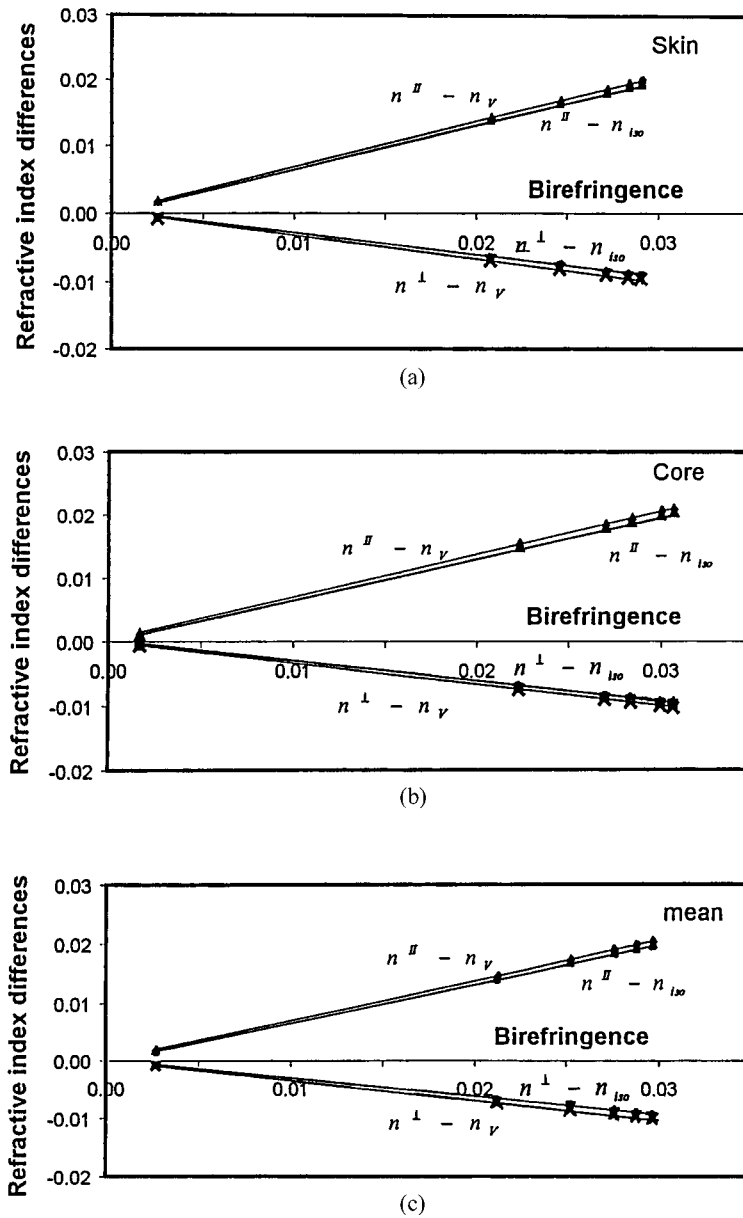Figure 5 shows the relation between the draw ratio and the orientation angle θ. It shows

Figure 4. Relation between the birefringence Δn and the refractive index differences ($n^{\parallel} - n_v$, $n^{\perp} - n_v$, $n^{\parallel} - n_{iso}$ and $n^{\perp} - n_{iso}$) at different draw ratios for (a) skin, (b) core and (c) mean refractive index values of PP fibres.

that the orientation angle is decreased by increasing draw ratio.

Figure 6 shows the variation of $\tan \beta$ with draw ratios. $\text{Tan } \beta$ decreases with increasing draw ratios for the mean, skin and core values.

Figure 7 shows the relation between optical orientation function $P_2(\theta)$ and the draw ratio, which shows an increase of $P_2(\theta)$ as draw ratio increases, and the skin has a higher optical orientation function.
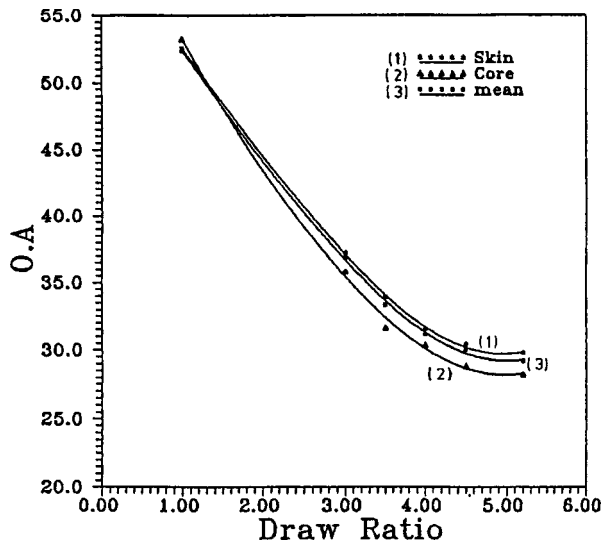
Figure 5. The angle of orientation as a function of draw ratio for the mean, skin and core values of PP fibres.
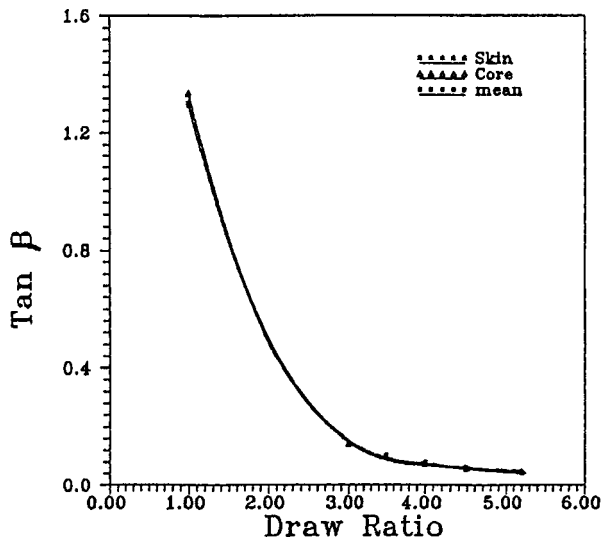

Figure 6. Relation between $\tan \beta$ and different draw ratio of PP fibres.

Figure 8 shows the linear relationship between the optical orientation function $P_2(\theta)$ and the value of $((\phi^\parallel - \phi^\perp)/(\phi^\parallel + 2\phi^\perp))$ for the mean, skin and core of a polypropylene fibre. The slope of this line gives the constant $(\Delta \alpha / 3\alpha_0)$ to be 0.025.

Figure 9 shows the relation between the random links per unit chain related to the undrawn fibre, N_c, and the draw ratio. N_c increases with increasing draw ratio.

Figure 10 shows the distribution of segments $\omega(\cos \theta)$ with respect to the draw ratio for the mean, skin and core of PP fibres.

The change in radius, r, of fibre due to the process of drawing is related to the change of the fibre length, l, according to the logarithmic Poisson ratio, μ [18], as defined by

$$\frac{\mathrm{d}r}{r} = \mu \frac{\mathrm{d}l}{l}. \tag{18}$$

The values of μ at different draw ratios are given in figure 11. It is clear that Poisson's
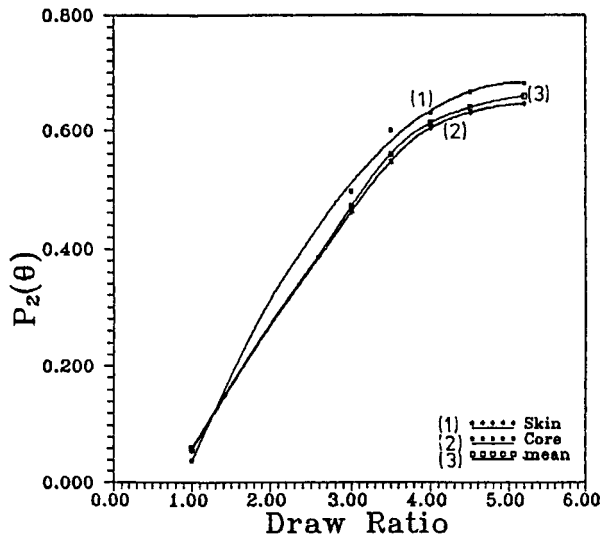
Figure 7. Relation between optical orientation function $P_2(\theta)$ for the mean, skin and core values of PP fibres.
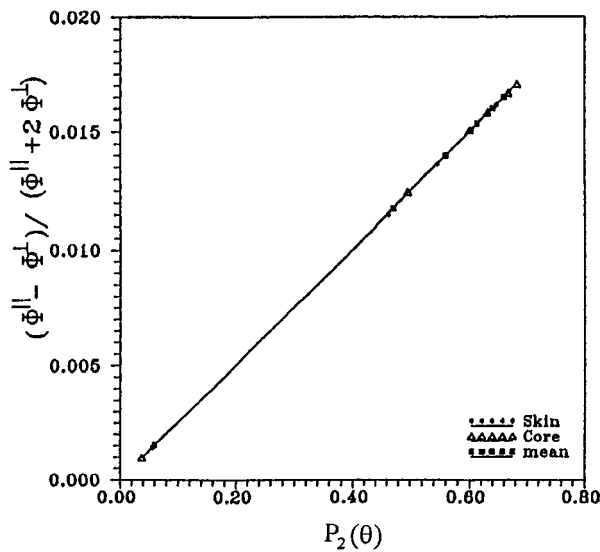

Figure 8. Relation between the optical orientation function $P_2(\theta)$ and the value $[(\Phi^{\parallel} - \Phi^{\perp})/(\Phi^{\parallel} + 2\Phi^{\perp})]$ of drawn PP fibres.

ratio decreases with increasing draw ratio. The strain optical coefficient, $C\varepsilon$, is defined as

$$C\varepsilon = \frac{\mathrm{d}\Delta n_a}{\mathrm{d}\varepsilon} \tag{19}$$

where ε is the strain and was determined for different draw ratios.

Figure 12 shows the variation of strain coefficient of drawn fibres related to undrawn fibre and the draw ratios.

4. Discussion

The drawing process is used to vary the degree of orientation, crystallinity and other physical properties in polymeric materials. Most properties are strongly influenced by chain orientation. Chain orientation is a purely geometrical quantity of a system. If the polymer segments have
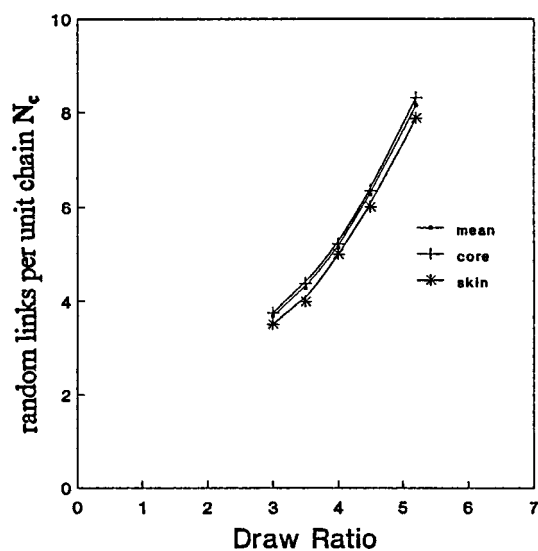
Figure 9. Relation between random links per unit chain N_c of drawn fibres (related to undrawn fibres) and draw ratio of PP fibres.
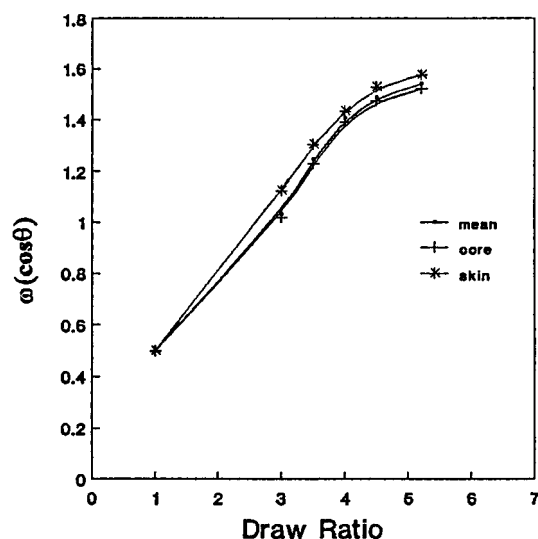

Figure 10. The distribution of segments at an angle θ with respect to the draw ratio for the mean, skin and core of PP fibres.

a preferential direction the system is said to be oriented. Chain (segmental) orientation can be determined by a number of methods, one of these methods measuring birefringence.

Orientation is the result of deformation. 'Mobile' molecules are extended by the application of an external force field (mechanical, electric or magnetic). The methods by which chain orientation is obtained may be divided into solid-state and liquid-state processes. The solid-state processes, i.e. cold drawing, extrusion or rolling, involve a plastic deformation of an isotropic or weakly anisotropic solid [19], so the study of mechanical properties of textile fibres. The author's aim is to establish a connection between the molecular structure and these properties and suggest beneficial modifications in the preparation or processing of the fibre [20].

So upon study of these drawn samples with different draw ratios, and following the obtained opto-mechanical parameters, we obtain a polymeric material with modified physical properties which can aid in the end use.
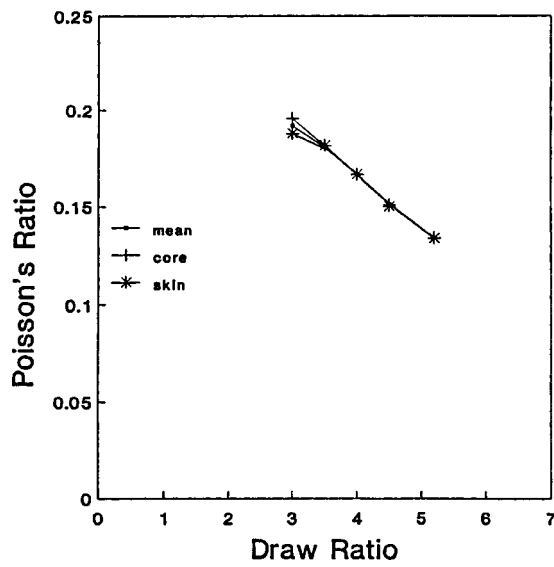
Figure 11. Relation between Poisson's ratio of drawn fibres (related to undrawn) and the draw ratio of PP fibres.
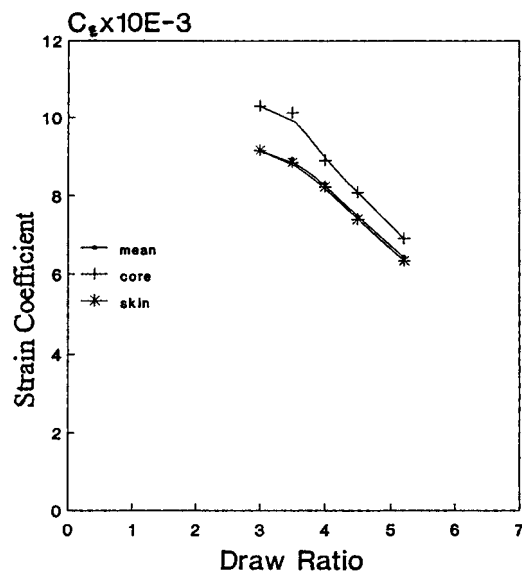

Figure 12. Relation between strain optical coefficient of drawn fibres (related to undrawn) and the draw ratio of PP fibres.

5. Conclusions

From the measurements and calculations relating the change of optical properties due to the drawing process for polypropylene fibres the following conclusions may be drawn.

(1) The microinterferograms clearly identify differences in optical path variations due to drawing processes and in the skin–core layers.

(2) The optical orientation function and the orientation angle are found to be affected by the drawing process (skin, core and mean layers). The orientation angles are found to decrease, while the orientation factors are found to increase (figures 5 and 7). The value $(\Delta\alpha/3\alpha_0)$, which depends upon the molecular structure, remains constant.

(3) The distribution function of segments increases with increasing draw ratio and varies from

0.5 to 1.6. Figure 10 indicates the mass redistribution associated with the drawing process of PP fibres, which gives new physical properties for the same polymer (i.e. dyeing, thermal, electrical etc).

(4) Poisson's ratio and strain optical coefficient are reduced by the strain effect.

(5) The higher the orientation function, the more mutually parallel the molecules and the smaller the average angle formed by them with the fibre axis, which in agreement with the obtained results for the decrease in orientation angle with increasing draw ratios.

We conclude from the above results and considerations that the practical importance of these measurements provides acceptable results for the opto-mechanical parameters Since $n_s^{\parallel}$, $n_s^{\perp}, n_c^{\parallel}, n_c^{\perp}, n_a^{\parallel}, n_a^{\perp}$ etc are a consequence of the material drawn, so reorientation of PP fibres may occur not only during fabrication but also after the fabrication process. Also it is acceptable that the multiple-beam technique is very promising to reveal the changes due to any physical deformation processes for study of the optical behaviour of the skin–core structure of any polymeric fibre.

Acknowledgment

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