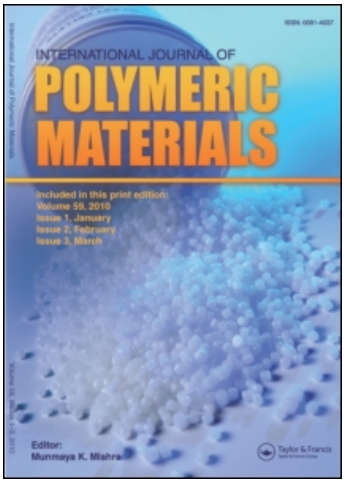

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Structure and Properties of Viscose Fibers due to Cold Drawing

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To cite this Article Fouda, I. M. , El-Khodary, A. and El-Sharkawy, F. M.(2007) 'Structure and Properties of Viscose Fibers due to Cold Drawing', International Journal of Polymeric Materials, 56: 10, 965 — 975
To link to this Article: DOI: 10.1080/00914030601163480
URL: http://dx.doi.org/10.1080/00914030601163480

International Journal of Polymeric Materials, 56:965–975, 2007

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030601163480

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Structure and Properties of Viscose Fibers due to Cold Drawing

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Viscose fibers (regenerated cellulose), were drawn using a stress-strain device, in conjunction with a two beam interferometric system. A recent approach is applied for determining the unknown initial value for a given viscose fiber. Optical and mechanical parameters were measured. The results were used to calculate the crystallinity, amorphous, and crystalline orientations functions. Calculation of the crosslink density and the chain entanglement density with the aid of Moony-Rivlin equation constants were given. Also, some other optical and mechanical structure parameters were given. An empirical formula is suggested for the results parameter changes. The present study throws light on the changes due to cold drawing processes for viscose fibers.

Keywords: birefringence, optical and mechanical parameters, orientation functions, viscose fibers

INTRODUCTION

An isotropic polymer has the same structure and properties in all directions. Upon deformation in the solid state, the polymer becomes anisotropic because the polymer chains align and therefore become oriented with respect to a particular direction. The degree of orientation with respect to a particular direction expresses a measure of the extent of anisotropy produced by the deformation process. Because the properties of an anisotropic polymer show a directional dependence,

Received 7 November 2006; in final form 4 December 2006.
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a measurement of the orientation in the polymer portrays how its properties are modified during deformation.

To measure the orientation in a polymer, there are a number of different techniques, depending on its constitution. The use of interferometric methods is one of considerable importance to provide information about the degree of orientation in a molecular system [1].

Viscose rayon filaments or fibers exhibit special microscopic characteristics. Because viscose rayon filaments and staple fiber are composed of regenerated cellulose, which has been coagulated and solidified from a solution of cellulose xanthate and are made in varying lusters and denier sizes, microscopic examination has been found to be the easiest, quickest, and most positive means of identification. According to available data, the cellulose chains in a rayon fiber do not lie in an entirely unoriented condition, but are partly oriented parallel to the fiber axis, depending on the degree of stretching to which they have been subjected. It has been found that mechanical, thermal, and chemical treatments may change the crystalline and amorphous parts in rayon fiber [2–6]. Freund and Mark [7] point out that the crystallized areas give to rayon a high modulus of elasticity, rigidity, and ultimate tensile strength whereas the amorphous parts are responsible for its flexibility, recovery, elongation, and swelling. If the internal mobility of the cellulose chains is increased by appropriate measures such as stretching, swelling, or a temperature increase, a certain amount of rearrangement will take place and the viscose rayon will undergo a change in its internal structure, in its external shape, and in its physical properties. Hence, viscose rayon is a very complicated system of certain intrinsic meta-stability that makes it very sensitive to any change of the external conditions. The complex structure of the interface between the crystallized and amorphous portions affects the setting properties.

The objective of this article was to study the effect of cold drawing processes on crystallinity, reduced stress, Moony-Rivlin constants, chain entanglement density, crosslink density, and initial value of the unknown draw ratio for the examined viscose fiber. Other optical and mechanical orientation parameters were also investigated.

THEORETICAL CONSIDERATION

The two-beam interference technique was used extensively [8–14] for determining optical parameters such as the refractive indices and birefringence namely $n_a^{\parallel}$, $n_a^{\perp}$ and Δn_a for different fibers, where $n_a^{\parallel}$ and $n_a^{\perp}$ are the mean refractive indices for light vibrating along and across the axis of the fiber and Δn_a is the birefringence. The principal

optical parameters were calculated using equations that were extensively used in several publications [9–11]. Also, the drawing process was studied as described elsewhere with the Pluta polarizing interference microscope connected to a mechanical device [12–14].

Optical Orientation Function

The total optical orientation function $F_{o.t.}$ was measured from the following equation [15]

$$F_{o.t.} = \frac{\Delta n}{\Delta n_{max}} \tag{1}$$

where Δn_{max} is the maximum birefringence of a fully oriented fiber. Its value was previously [15] determined to be 0.055.

Mechanical Orientation Function

The low-strain mechanical anisotropy is related to the orientation function $P_2(\cos\theta)$, which is equal to the total mechanical orientation function, F_{tot}. This function provides some understanding of the mechanism of deformation. By considering the network as freely jointed chains of identical links, called random links, F_{tot} is given by [16]

$$F_{tot} = \frac{1}{2}\left[\frac{(2+U^2)}{(1-U^2)} - \frac{(3U\cos^{-1}U)}{(1-U^2)^{3/2}}\right] \tag{2}$$

where $U = D^{-3/2}$ and D is the draw ratio.

Isotropic Refractive Index

Because most macromolecular crystals are birefringent, an appropriate average refractive index [17] must be used and can be given by the following equation:

$$n_{iso} = (n_{\perp}^2 n_{||})^{1/3} \tag{3}$$

EXPERIMENTAL

Material

The viscose fibers are manufactured by Misr Rayon Co. The untreated samples had T_g of 45.9°C and crystallinity was 46.19%.

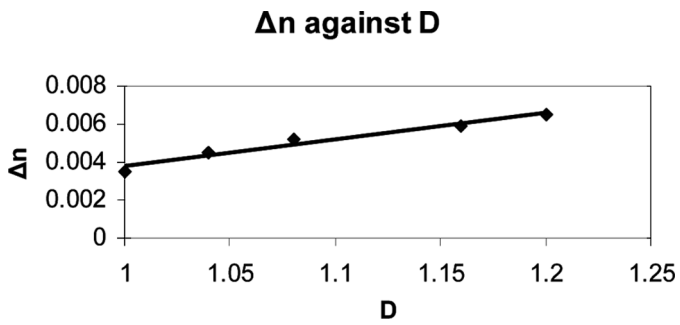

FIGURE 1 The relationship among the birefringence of viscose fiber (Δn) and the draw ratio (D).

The Initial Value of Unknown Draw Ratio for Any Fiber

To estimate the initial draw ratio D_o of any given fiber sample, the refractive indices, and hence the birefringence, are determined using the opto-mechanical system that was designed and discussed in detail previously [18]. Plotting the birefringence as function of the draw ratio leads to a straight line whose equation in the form $\Delta n = A + B(D + D_o)$, where D is the experimental draw ratio. For a non-drawn fiber ($D = 1$), one may consider the fiber medium is isotropic, that is, $\Delta n = 0$. Introducing these characteristic values into the linear equation, one obtains the real value of D_o. Also, the extrapolation of the line Δn vs. D should cut the negative part of the axis (D) at D_o. So the actual draw ratio was found to be $(D + 0.7266)$ as shown in Figure 1.

Optical Sectional Area for Viscose Fiber

The cross-section of viscose fiber has been seen by a high power optical microscope [19] and was found to be of irregular shape of area $1.165 \pm 0.2\,mm^2$.

Double Beam Interferometry

Viscose fiber was examined by the double beam Pluta interference microscope connected to stress-strain device using plane polarized light.

Crystallinity

As is well known [20], n_{iso} is linearly proportional to the density and the density shows a linear dependence on the crystallinity X_c, which

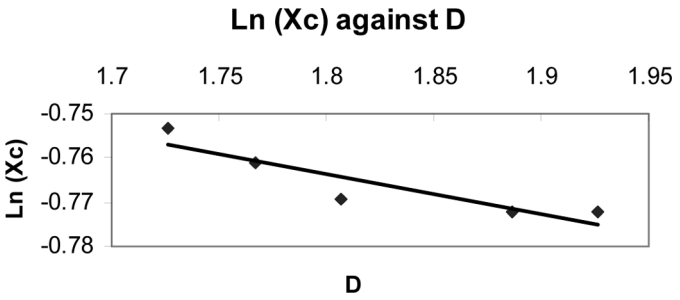

FIGURE 2 The dependence of the crystallinity (X_c) of viscose fiber on the draw ratio (D).

is estimated by [21]:

$$X_c = \frac{[n_{iso} - n_{iso}(X_c = 0\%)]}{[n_{iso}(X_c = 100\%) - n_{iso}(X_c = 0\%)]} \tag{4}$$

where n_{iso} ($X_c = 0\%$) and n_{iso} ($X_c = 100\%$) are the values for ideal amorphous solid ($X_c = 0\%$) and crystalline states ($X_c = 100\%$), respectively. These two quantities can not be directly evaluated by experiments because of the difficulty of preparing the samples of $X_c = 0\%$ and 100%. Thus these were only indirectly estimated in such a manner that the X_c calculated from observed values of n_{iso} for a widest variety of test samples between 0 and 100%. The values of n_{iso} ($X_c = 0\%$) and n_{iso} ($X_c = 100\%$) thus obtained are 1.5077 and 1.5533, respectively. Eq. 4, can be rewritten for the regenerated celluloses in the form

$$X_c = \frac{(n_{iso} - 1.5077)}{(1.5533 - 1.5077)} \tag{5}$$

This equation allows used of n_{iso} to evaluate X_c as is clear in Figure 2, while X_c results are given in Table 1.

Orientation Functions

Using the estimated value of the crystallinity, one can then calculate the value of the orientation functions of the amorphous phase according to

$$F_a = \frac{(F_{tot} - X_c F_c)}{(1 - X_c)} \tag{6a}$$

TABLE 1 Values of D, Δn, n_{iso}, X_c, different orientation functions, σ and σ^*

D	Δn	n_{iso}	X_c	F_c	F_{tot}	Fo.t.	F_a	σ	σ^*
1.7266	0.0035	1.5292	0.4707	0.5803	0.3430	0.0636	0.1320	–	–
1.7666	0.0045	1.5290	0.4671	0.6007	0.3570	0.0818	0.1434	3.54	4.8450
1.8066	0.0052	1.5288	0.4634	0.6201	0.3706	0.0945	0.1551	5.67	7.7602
1.8866	0.0059	1.5288	0.4619	0.6558	0.3965	0.1073	0.1739	7.81	10.6891
1.9266	0.0065	1.5288	0.4619	0.6722	0.4089	0.1182	0.1828	9.46	12.9474

σ and σ^* are in MPa.

where F_{tot} is the total orientation function and F_a and F_c are the orientation functions of the amorphous and crystalline regions, respectively.

The orientation factors crystallites F_c were evaluated using the following equation:

$$F_c = \frac{(D^3 - 1)}{(D^3 + 2)} \tag{6b}$$

where D is the draw ratio. F_c, F_{tot}, and F_a are given in Table 1 and shown in Figures 3-5.

Moony-Rivlin Constants [22]

To fit the Ball model [23] to the experimental data, initial estimates of the model parameters are needed. These were obtained using Moony-Rivlin plots where the reduced stress

$$\sigma^* = \frac{\sigma}{(D_{max}^2 - D_{min}^2)} \tag{7}$$

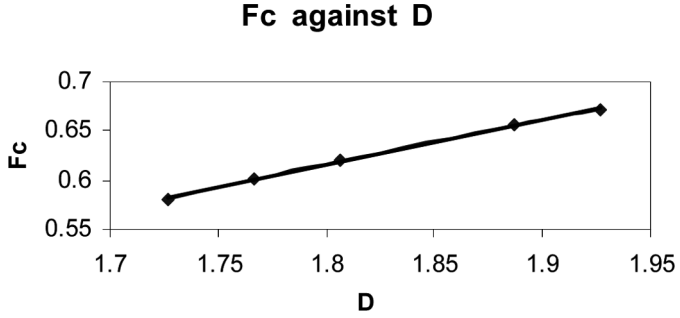

FIGURE 3 The dependence of the crystalline orientation (F_c) of viscose fiber on the draw ratio (D).

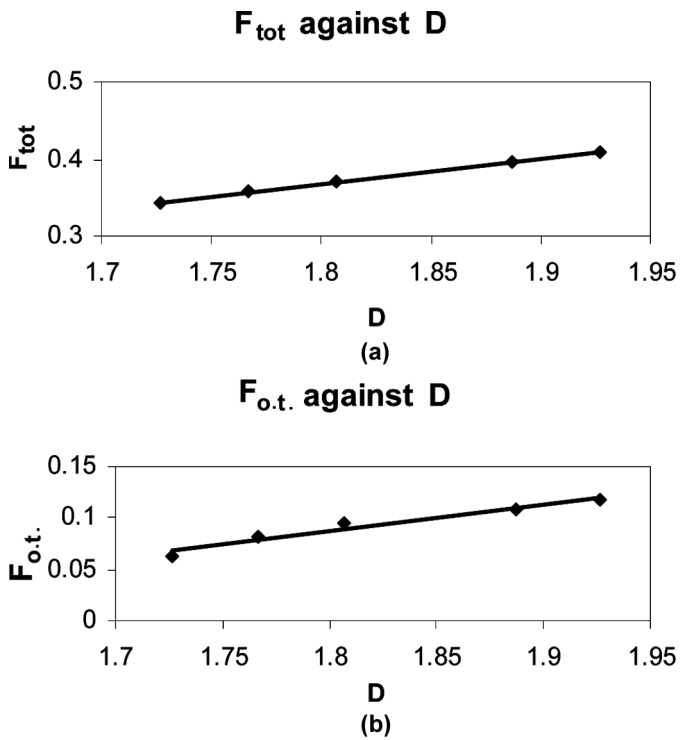

FIGURE 4 (a) The variation of the (F_{tot}) of viscose fiber with the draw ratio (D). (b) The variation of the ($F_{o.t.}$) of viscose fiber with the draw ratio (D).

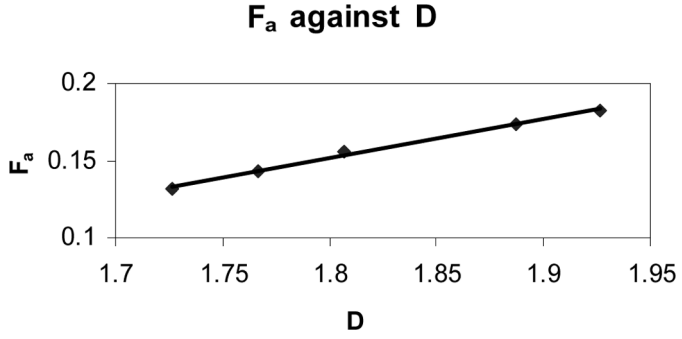

FIGURE 5 The variation of the amorphous orientation (F_a) with the draw ratio (D).

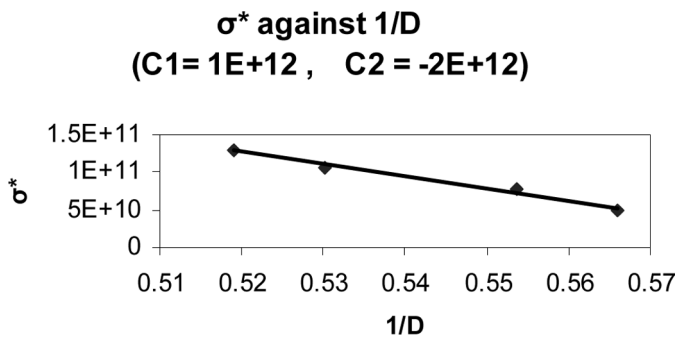

FIGURE 6 The variation of the reduced stress (σ^*) with the inverse of the draw ratio (1/D) of viscose fiber.

is plotted against the inverse of the draw ratio, which gives a linear plot for rubber-like behavior as shown in Figure 6. Therefore

$$\sigma^* = (C_1 + C_2 D^{-1}) \tag{8}$$

where C_1 and C_2 are empirical constants called the Moony-Rivlin coefficients, which can be related, approximately, to the structure of the network parameters, N_o, the crosslink density and N_s, the chain entanglement density,

$$N_o = \frac{C_1}{kT} \tag{9a}$$

$$N_s = \frac{C_2}{kT} \tag{9b}$$

where k = Boltzmann's constant and T is the absolute temperature. The estimate of N_s, however, is not strictly correct because C_2 also relates to the link effectiveness. As Moony-Rivlin plots obtained from the deformation of viscose fiber are not linear over the whole strain range, only the data points on the initial linear part of the curve were used to give values of $N_o = 2.4143 \times 10^{+25}$ and $N_s = -4.8287 \times 10^{+25}$.

RESULTS AND DISCUSSION

Viscose rayon filaments or fibers exhibit special microscopic characteristics. The viscose rayon filaments and staple fiber are composed of regenerated cellulose that has been coagulated and solidified from a solution of cellulose xanthate and are made in varying states. Microscopic and interferometic techniques have been found to be

the quickest, easiest, and most positive means of identifications. So the structure complexity undoubtedly originates from the existence of a wide variety of the intra- and intermolecular hydrogen bondings in the cellulose solid [24–26]. For example, the degree of crystallinity obtained for a given regenerated cellulose solid is not always the same, but depends significantly on the method of measurements employed [27]. So the degree of orientation, crystallinity, and other structural parameters are correlated to the final fiber end use. Much effort has gone toward clarifying the molecular orientation characteristics of semi-crystalline polymers, which usually form not only a crystalline phase but also an amorphous solid phase. As the degree of orientation always increases in the course of drawing, the crystallinity can change in both directions. Three types of behavior can be distinguished [28]:

1. Deformation is accompanied by an increase of crystallization.
2. Deformation does not affect the degree of crystallinity.
3. Deformation is accompanied by a reduction of crystallinity.

Thus, the present results show that deformation was accompanied by a reduction of crystallinity as shown in Figure 2. The reduction in the degree of crystallinity of the original fiber assists in dying and swelling processes due to increase of the amorphous areas. The drawing of viscose fiber produces reorientation of the mass distribution as is clear from the increase of F_c, F_{tot}, and F_a in Figures 3–5, respectively. Thus the present results show a reduction of the crystallinity, which may be due to drastic distortion of the original structure of the amorphous material due to cold drawing [10]. Table 1 gives some experimental results of D, Δn, n_{iso}, X_c, F_c, F_{tot}, $F_{o.t.}$, F_a, σ and σ^*. The following empirical formula is suggested to evaluate the relationship between crystallinity, orientation functions, birefringence, and reduced strain with the draw ratios: $\mathrm{Ln}(X_c)F_cF_a\ \Delta n/\sigma^* = CD + Y$, where C and Y are constants characterizing the proportionality between $\mathrm{Ln}(X_c)\ F_c\ F_a\ \Delta n/\sigma^*$ and D. The values of C and Y vary with the drawing ratio and were found to be 7×10^{-15} and -2×10^{-14}.

CONCLUSION

It is clear that the two-beam technique in conjunction with a microstrain device is useful to clarify the opto-mechanical behavior of viscose fibers. From the obtained results the following conclusions are reported:

1. Crystalline and amorphous orientation functions (F_c and F_a) increased as the draw ratios increased (Figures 3 and 5) and also $F_{o.t.}$ and F_{tot} increased. So changes in orientation are accompanied by changes due to cold drawing process. This indicates mass redistribution within the fiber.
2. The crosslink density (N_o) and the chain entanglement density (N_s) were calculated as the draw ratio increased and were found to be $N_o = 2.4143 \times 10^{+25}$ and $N_s = -4.8287 \times 10^{+25}$.
3. Crystallinity decreases as draw ratio increases and depends greatly on the energy of the intermolecular interactions, which affects the molecular motion in viscose fibers.
4. Empirical formula is suggested to correlate the changes with different draw ratios and constants of 7×10^{-15} and -2×10^{-14}.

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