The Behavior of Spiral Angle ϕ and the Angle of Crystallite Dispersion α of Normal Cottons with Stress

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Synopsis

It is well known that the cotton fiber consists of microfibrils which in turn do have crystalline and amorphous regions. The crystallites are arranged in the form of helices, and with stress the helical configuration changes. This paper examines the configurational changes that occur in the helix and makes it clear that the amorphous regions of the microfibrils are the source of these changes.

INTRODUCTION

The polymer organization of native cellulose in cotton has generally been described in terms of the fringed micellar theory wherein the microfibrils are arranged in an order parallel to the fiber axis. The microfibrils are, in turn, an assembly of crystalline and amorphous regions. The bulk of this cellulose substrate is seen in the S2 layer where there is a helical orientation of molecules and fibrils. The helix angle of the crystallites of the molecules about the fiber axis is generally known as the spiral angle. Along the length of the fiber at intervals the sense of the helix reverses. Peterlin and Ingram[1] have pointed out the microfibrillar crystallite helices as one of the principal elements providing the bulk of the mechanical properties of the cotton fiber. Thus, it would be worthwhile to investigate the spiral angle of the crystallites with stress so that one may get a lead to identify the structural elements determining the mechanical properties of the cotton fiber.

The degree of alignment of the crystallites along the fiber axis is known as the orientation of the fiber. Clark[2] was the first to measure this orientation. Hermans et al.[3] have developed a mathematical expression to quantify this preferred orientation, and Segal et al.[4] and Creely and Conrad[5] have developed a diffractometric technique for its evaluation. Deluca and Orr[6,7] have interpreted the X-ray diffraction of cotton in terms of the orientation of the fiber structure. Their mathematical interpretation is based on the assumption that the azimuthal intensity scan around the diffraction arc can be regarded as the sum of two Gaussian distributions separated by the spiral angle and the width of the individual distribution being the angle of crystallite dispersion about the fibril axis. Thus by this method the analysis of both the spiral angle and the orientation angle in the fibrils about the fibril axis is possible.

When a fiber is subjected to tension, the microfibrils are the elements which ultimately bear the load. Therefore, it would be of great interest

Journal of Applied Polymer Science, Vol. 30, 3801–3807 (1985)
 CCC 0021-8995/85/093801-07$04.00

to know how these internal parameters vary with applied stress. Kalyanaraman[8-11] has investigated this property and has described a certain type of relations with X-ray angle, spiral angle, and orientation angle etc. This paper summarizes the relationships between elongation and stress developed with the spiral angle and the angle of crystallite dispersion.

EXPERIMENTAL

Twenty-one cottons of American origin are taken. A random sample of each cotton is taken, and they are combed using fibrograph combs. Thus one set of parallel tuft is made, and, using the same, a good bundle is made. The bundle preparation is described in detail in earlier work.[9,10] The bundle is now mounted on to a special device fabricated by Kalyanaraman and Ramakrishnan.[8] This has a special feature that one could determine the X-ray orientation both before and after stretching and is capable of being mounted on to the X-ray diffractometer as well as the instron tensile testing setup. In the present investigation, the orientation factor is estimated by using the diatropic (040) diffraction. The methods are discussed in detail by Kalyanaraman.[10,12]

The bundles are mounted on to the texture goniometer setup of the X-ray diffractometer and the orientation factors are measured by employing a pulse height discriminator and proportional counter. Point to point counting technique is used.

To start with, the 040 diffraction is located at 2θ equal to 34.5° and the azimuthal scan is made on either side of the diffraction center. From the zero position, the azimuthal scan of the intensity is obtained by counting the intensity from 0 to 90° on either side at equal intervals of 3° and for a fixed time of 32 s. The mean of the corresponding values on either side is chosen for the calculations. The background noise is assumed to be linear and is equal to the intensity observed at azimuth equal to 90°. This assumption is correct, since there are no other diffraction in the vicinity of the reciprocal space of 040 and, thus, there is no contamination in the background. The background noise is estimated on both sides, and it is substracted from the intensity values obtained. To estimate the spiral angle, the azimuthal intensities at 15 and 30° are noted on both sides of the peak, and the average is used for the calculation. Ni-filtered CuKα is used for the entire investigation.

After making the azimuthal scan and estimating the parameters required for the calculations, the bundle is transferred to the instron machine and is subjected to an extension for 30 s. The bundles made for the investigation had an approximate length of 10 mm and the crosshead of the instron machine was moved at a constant rate of 0.5 mm/min, which is the slowest possible speed available in the unit. The movement is arrested exactly after a lapse of 30 s, which would roughly correspond to 2% extension of the fiber bundle. After the necessary extension has been achieved, the bundle is frozen from further extension and is transferred to the X-ray goniometer for further azimuthal scan and measurements. Extensions of 4, 6, 8, and 10% are planned during the investigation. However, even before the onset

of the fifth extension, some fibers show breakage, and, under such circumstances, the investigation has been stopped with the fourth stage or so.

For each state of extension, a new bundle is used, since an already extended bundle could by the passage of time lead to relaxation phenomena. For each extension, a minimum of two bundles is used, and thus, for each cotton, the observations are made on two bundles on the average. The readings required for the measurement of orientation and for the calculation of spiral angle is noted on each bundle for each extension.

All the experiments have been done under the laboratory conditions with the temperature at 27 $\pm$ 2°C and relative humidity at 65 $\pm$ 2%.

The spiral angle and the angle of crystallite dispersion are calculated as per Deluca–Orr procedure as outlined by Kalyanaraman.[12] The calculations are done by the program written by the author for the IBM 370 machine.

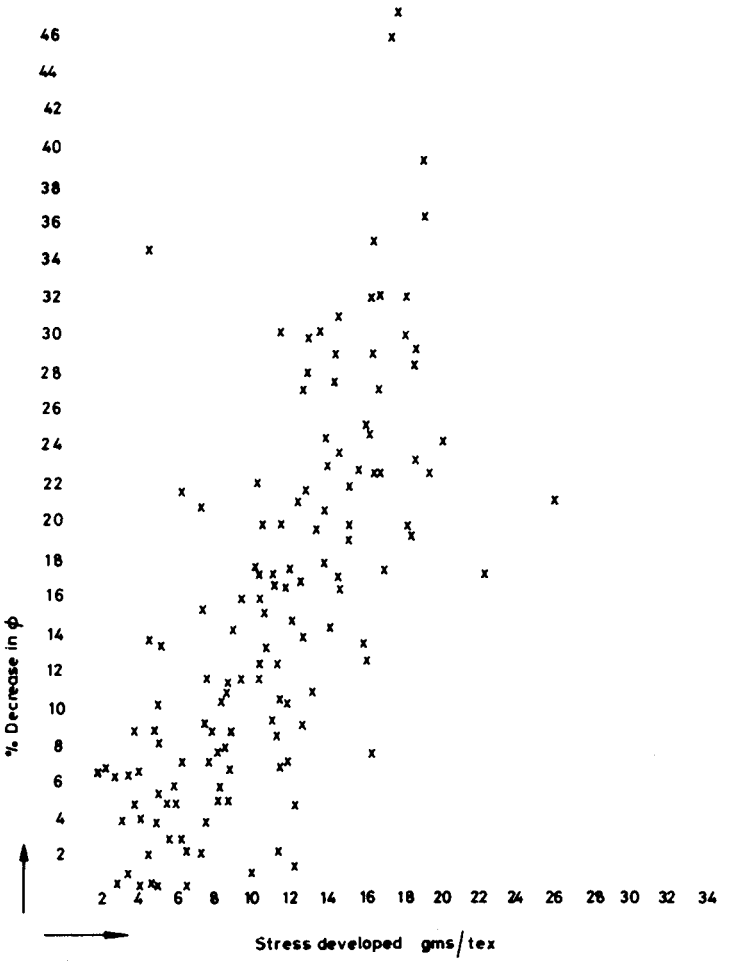

Fig. 1(a). The percentage decrease of the spiral angle with increase in stress.

DISCUSSION

The stress developed, increase in orientation, change in spiral angle, and change in angle of crystallite dispersion for all the cottons are given in the earlier work.[9,10] Since several bundles have been used and each bundle may have a different set of fibers, it has been decided to investigate the change in properties in terms of the percentages. Such a procedure would possibly eliminate the disparity that might arise due to the bundle to bundle variation.

Figure 1(a) represents stress developed vs. the spiral angle ϕ. As stress increases, the spiral angle comes down. This means that, with stress, the microfibrils are aligning themselves towards the fiber axis as has been pointed out by Peterlin and Ingram.[1] The variation of ϕ with stress developed seem to be regular.

Stress developed versus α is not ordered and the variation is haphazard, as is seen from Figure 1(b). This means that the crystallites themselves do

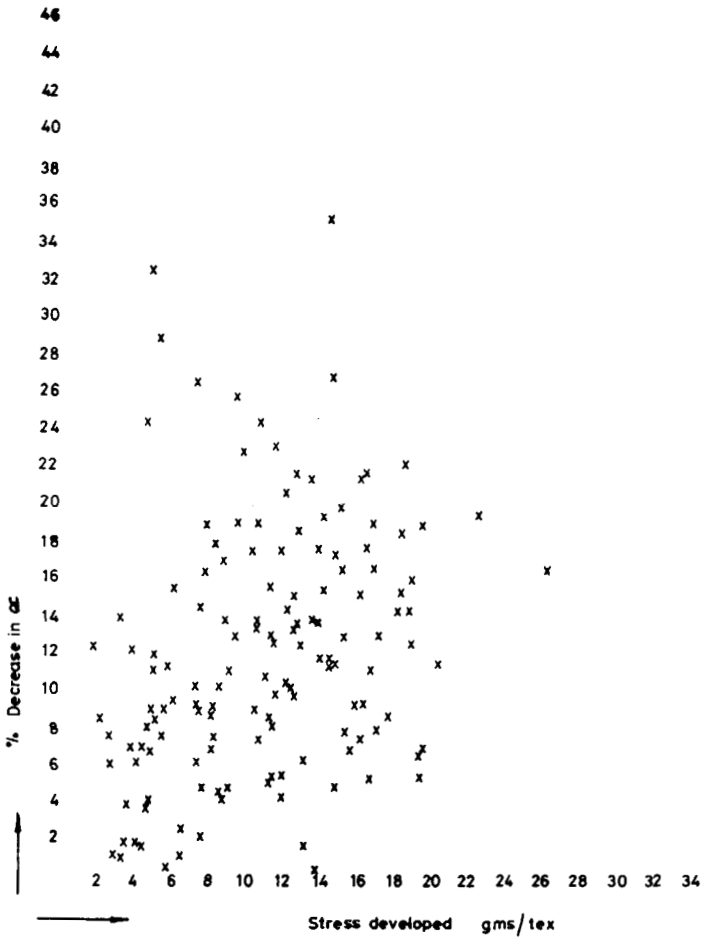

Fig. 1(b). The percentage decrease of angle of crystallite dispersion with increase in stress.

not partake in the elastic behavior of the fibers. However, the amorphous regions in between the crystallites do change due to the change in the spiral angle, and the crystallites realign themselves so as to break old hydrogen bonds and make new ones to contribute towards minimum energy configuration. The fact that the diffraction does not change with stress, which is quite contrary to what is seen in metals implies that the crystallites do preserve the lattice order and change takes place only in the amorphous regions. Thus stress seems to affect only the amorphous region.

Figure 2(a) and 2(b) represent the increase in elongation percentage with decrease in spiral angle π and the angle of crystallite dispersion. These relations also appear to be linear. However, the angle of crystallite dispersion shows slightly more scatter than the other. This signifies that elongation is contributed more by realignment of helices and partly by the crystallites readjusting themselves. Thus, this investigation supports the

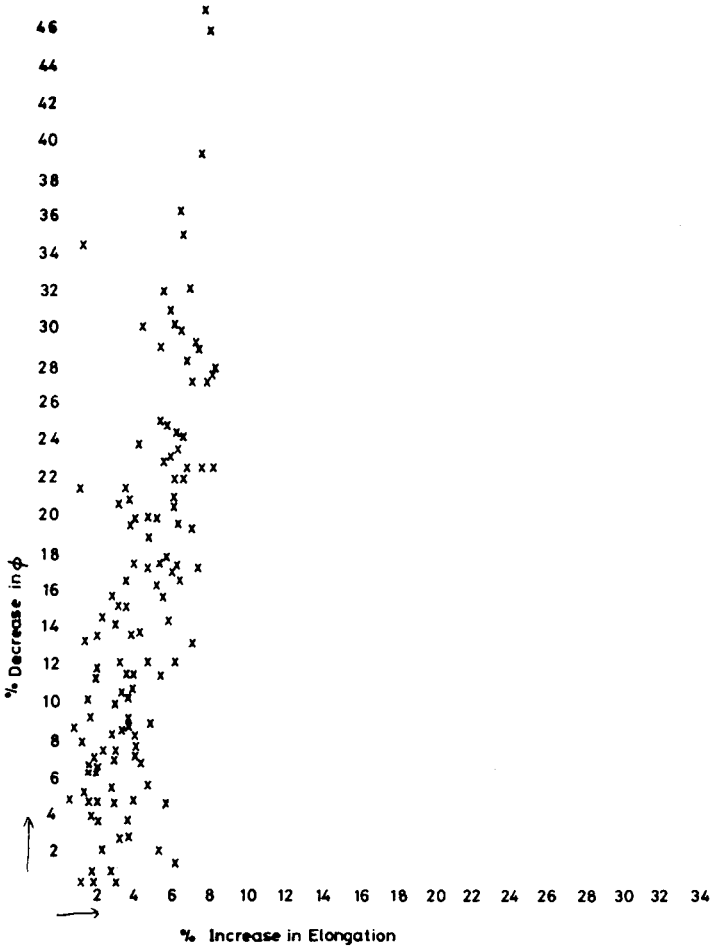

Fig. 2(a). The percentage decrease in the spiral angle with percentage increase in elongation.

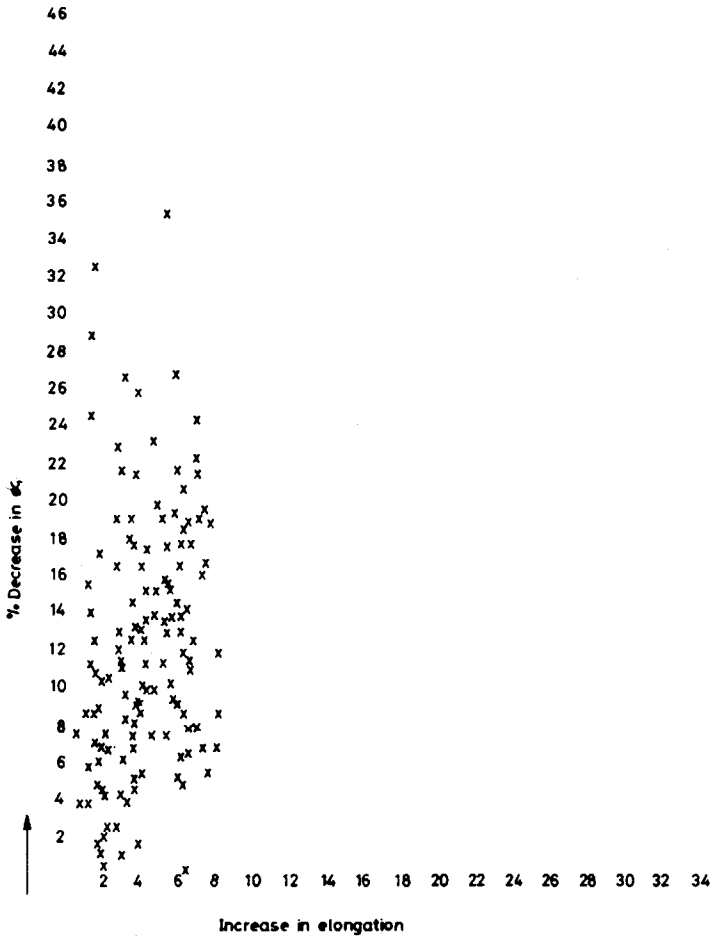

Fig. 2(b). The percentage decrease in angle of crystallite dispersion with percentage increase in elongation.

crystalline amorphous structure of cellulose fibrils and explains their role when the fiber is stressed.

Also it is interesting to note that about an 8% variation in elongation could nearly bring about 50% variation in ϕ [Fig. 2(a)] and a similar variation of 50% in X-ray angle. This is also in order since spiral angle and 50% X-ray angle are related to each other as pointed out by Kalyanaraman[10] earlier.

CONCLUSIONS

1. With stress, the crystallite structure is not disrupted.

2. With stress, the variation of the spiral angle is regular whereas the variation of the angle of crystallite dispersion is haphazard. This means that the amorphous regions of the microfibrils are the source of these changes while the crystalline remains unchanged.

3. The amorphous regions are those that contribute towards the elastic

nature of the fibers or, in other words, highly crystalline fibers would be brittle.

LIMITATIONS

This investigation is done on bundles and since combed bundles are used the conclusions are the results averaged over a limited population of the fiber sample. Also this paper assumes that 040 diffraction is made up of two overlapping distributions, which are resolved by the Deluca–Orr procedure. They may be cited as a limit of the scope of the present investigation. However, the examination of the final properties reveal that the above procedure is reasonable as it agrees with several conclusions arrived at by earlier workers by totally different types of methods.

The author thanks Mr. R. R. Ramakrishnan for the collection of data and calculations, Mr. T. V. Ratnam, Director, SITRA for his kind encouragement and interest in the work and the Agricultural Research Service, United States Department of Agriculture, for financial support.

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Received September 27, 1984
Accepted February 5, 1985