In this paper, the influence of fiber dyeing on the internal structure of cotton fibers was investigated. For this purpose, some cotton fibers originating from growing areas in the Aegean region and around Kahramanmaraş city in the Mediterranean region were used. The physical properties of the cotton fibers were characterized by an Uster HVI 1000 Instrument. Whole cotton fibers were pretreated, dyed and washed using the same process parameters. The inner structures of undyed and dyed cotton fibers were analyzed by the X-ray diffraction method. The peak positions, full width at the half-height of maximum peaks (FWHM) ($\beta$) and d-spaces of cotton fibers were obtained by X-ray diffraction. Crystal sizes were calculated using Scherrer’s equation. The crystal sizes, $\beta$ and d-spaces of undyed and dyed cotton fibers were compared. It was found that the inner structure parameters of the cotton fibers were altered after the dyeing processes.

Keywords: cotton fiber, fiber dyeing, reactive dye, inner structure, X-ray diffraction, crystal size, d-spacing

INTRODUCTION

Cotton is, by far, the most important and dominant natural textile fiber. Now, it is only exceeded in volume by polyester fiber.\textsuperscript{1-4} In 2015, the ratios of cotton and polyester fibers in global fiber consumption were around 27% and 55%, respectively (Fig. 1).\textsuperscript{4}

Cotton is the purest source of cellulose. Cotton fibers mainly consist of $\alpha$-cellulose (88-96.5%). Cotton cellulose has high molecular weight and structural order, i.e., it is highly crystalline, oriented and fibrillar. Cotton, with this high availability and structural order of the most abundant natural polymer, is, not surprisingly, viewed as a premier fiber and biomass.\textsuperscript{5}

Cellulose is a linear syndiotactic homopolymer, composed of D-anhydroglucopyranose units, which are linked together by $\beta$-(1→4)-glycosidic bonds. Each anhydroglucose unit includes three hydroxyl groups, one primary on C-6 and two secondary on C-2 and C-3. The abundant hydroxyl groups and the chain conformation allow extensive intra-molecular and inter-molecular hydrogen bonding to further increase the rigidity of the structure of cellulose. Hydroxyl groups also allow for dye molecules to form bonds.\textsuperscript{5,8}

The fine structure of native cellulose fibers has important implications in the biological processes of plant growth, chemical or enzymatic transformation of cellulosic biomass, as well as for the conception of new materials and understanding of physical properties of a wide range of cellulose-based materials.\textsuperscript{9} Molecular modeling of the chain conformation of cellulose and the settlement of cellulose in the base centered monoclinic unit cell are shown in Figure 2 (a)\textsuperscript{10} and (b),\textsuperscript{11-12} respectively. The effects of heating and chemical reactions on cotton cellulose depend on its super-molecular structure, as well as on the activity of the C-2, C-3 and C-6 hydroxyl groups. Chemical reactions or heating effects start in the more accessible amorphous region and the surfaces of crystalline domains.\textsuperscript{5}
Dyes may be defined as substances that, when applied to a substrate, provide color by a process that alters, at least temporarily, some crystal structure of the colored substances. Reactive dyes are dyes that form a covalent bond with cotton fibers. The key parts of the dye molecule are the chromophore and the reactive group. Reactive dye is one of the most widely used synthetic dyes for cotton dyeing, owing to its wide color gamut, brilliant color, excellent wet-fastness and easy application.

Cotton fabrics are highly popular due to their excellent properties, such as versatility, softness, hygroscopicity, breathability, affinity to skin, biodegradability and regeneration property. Colored cotton fibers are mostly used in fancy yarn production. Among the types of fancy yarn, mélangé yarn is known for its attractive color and appearance. Mélangé yarn is a type of spun yarn made from two or more fiber groups with different colors or dye affinities.

The aim of this research was to describe the structure of Turkish cotton fibers before and after dyeing processes. The structural parameters play an important role in determining both physical and chemical properties of textile fibers. Therefore, it is important to recognize the structural properties of cotton fibers before using them in textile production. Turkey is one of the major cotton-producing countries in the world. For this reason, the investigation of the structure of Turkish cotton fibers is very important. In this study, which is part of a more extensive work, the inner structures of raw and dyed cotton fibers were examined. The dyeing properties of different cotton types, another part of this comprehensive project, will be examined in another paper.

**EXPERIMENTAL**

**Materials**

The cotton fiber samples used in this research were collected from some cotton varieties grown in different locations of the Aegean region and Kahramanmaraş city and its environs. These cotton fiber samples were varieties of Aksel, Carmen, Celia and Flora (the Aegean region) and varieties of Adana-98, BA-308 and Stoneville-453 (Kahramanmaraş city and its environs). From these cotton samples, Carmen and Adana-98 cottons were registered at Nazilli Cotton Research Center in Turkey.

In the processes of pretreatment, dyeing and washing, a wetting agent (Torawet SK-37), a degreasing agent (Weltex PY), sodium hydroxide (NaOH), a stabilizer (Iyonex Fe), hydrogen peroxide (H₂O₂), acetic acid (CH₃COOH), antiper enzyme (Perozym HO CONC), salt (Na₂SO₄), soda (Na₂CO₃) and reactive dye (Synozol Gold Yellow HF-2 Gr 150) were used.
Methods
In this research, the same processes of pretreatment, dyeing and washing were applied for all the cotton fibers. Thus, the effect of the parameters of these processes was excluded.

The conditions and prescriptions for the pretreatment, dyeing and washing processes applied to the cotton fibers were taken from the industrial manufacturing process used at ÇMS Tekstil San. Tic. A.Ş., based in Kahramanmaraş, in Turkey. These processes were performed by an ATAC Lab Dye HT laboratory scale dyeing machine.

Pretreatment processes of cotton fibers
The cotton fiber samples were pretreated according to the recipe and conditions given in Figure 3. Wetting agent (1 g/L), degreasing agent (0.5 g/L), NaOH (3 g/L), stabilizer (1 g/L), H2O2 (5 g/L), acetic acid (0.5 g/L) and antiper enzyme (0.15 g/L) were used in the pretreatment processes of cotton fibers. The liquor ratio of the pretreatment bath was 1:7. The same prescription, conditions and chemicals were used for all cotton fibers. In the first bath (Fig. 3 a), cotton fibers were bleached using H2O2 at pH 10-11 and a temperature of 100 ºC. In the second bath (Fig. 3 b), rinsing was carried out for 10 minutes at 80 ºC. In the third bath (Fig. 3 c), using acetic acid, the pH was adjusted to 5, which the most suitable for the antiper enzyme, and the remaining H2O2 was removed.

Dyeing processes of cotton fibers
Pretreated cotton fibers were dyed according to the recipe and conditions given in Figure 4. Reactive dye (1%), salt (40 g/L), wetting agent (1 g/L) and soda (20 g/L) were used in the dyeing process. The dyeing process of cotton fibers was carried out as shown in the flowchart in Figure 4.

Washing processes of cotton fibers
After the dyeing process, the cotton fiber samples were washed, neutralized and softened according to the conditions given in Figure 5.
Measurement of physical properties

The physical properties of the cotton fibers were measured by using a High Volume Instrument (Uster HVI 1000).

Wide-angle X-ray diffraction (WAXD)

Cotton fiber powder from each sample was placed into a specimen holder. A Panalyt X’Pert PRO X-ray diffractometer was employed to obtain the X-ray diffraction patterns of the investigated cotton fiber samples. CuKα (λ = 1.5406 Å) radiation was generated at an accelerating potential of 40 kV and a tube current of 30 mA. Diffraction intensities were counted at 2°/min scanning speed, in the two theta (2θ) angle range from 5° to 45°.

For each fiber sample, the peak positions, interplanar d-spacings and the full width at half-height of the maximum peaks (FWHM) (β) were obtained by the X-ray diffractometer. Average crystal sizes (tc) were calculated from the X-ray graphics, using the Scherrer equation (Eq. 1).22 24 Peak breadths can provide information on both the crystallite size and on the disorder. The Scherrer equation (Eq. 1) relates the minimum crystallite size tc to the breadth.24

\[ t_c = \frac{K \lambda}{\beta \cos \theta} \quad (1) \]

where \( t_c \) is crystal size, \( K \) is the “shape factor”, \( \lambda \) (= 1.5406 nm) is the wavelength, \( \beta \) is the full width of peak at the half-height (rad), \( \theta \) is peak position in the diffraction pattern (half of the 2θ value). The value of \( K \) often gives values of about 0.9, but can range from 0.6 to 2.08.

RESULTS AND DISCUSSION

The spinning consistency index (SCI), micronaire (Mic), maturity index (Mat), fiber length (Len), fiber amount (Amt), fiber uniformity index (Unf), short fiber index (SFI), fiber strength (STR), fiber elongation (Elg), moisture (Moist), reflectance degree (Rd), yellowness (+b), trash count (Tr Cnt), trash area (Tr Area) and trash grade (Tr Grade) values of the cotton fibers measured by Uster HVI-1000 are given in Table 1. The most important physical property of cotton fibers for the dyeing process is maturity. The maturity index of cotton fibers used in the study varies about between 0.85 and 0.93.25 According to Uster technologies, maturity index values between 0.86 and 0.95 refer to mature cotton fibers. As a result, all cotton fibers, except Celia, are mature cotton fibers.

Table 1

HVI Test results of cotton fibers

| Fiber     | SCI   | Mic   | Mat | Len | Amt | Unf | SFI | STR | Elg | Moist | Rd  | +b | Tr Cnt | Tr Area | Tr Grade |
|-----------|-------|-------|-----|-----|-----|-----|-----|-----|-----|-------|-----|----|--------|---------|----------|
| Adana-98  | Mean  | 176   | 4.57| 0.92| 29.83| 752 | 86.0| 6.5 | 36.9| 5.6   | 7.6 | 81.9| 7.0    | 24      | 0.22     |
|           | S.D.  | 6     | 0.09| 0.01| 0.17| 11  | 0.7 | 0.1 | 1.2 | 0.3   | 0.1 | 0.1 | 0.1    | 0.3     | 0.01     |
|           | CV %  | 3.6   | 1.9 | 1.1 | 0.6 | 1.3 | 0.8 | 0.9 | 3.3 | 5.4   | 0.1 | 0.8 | 12.9   | 4.5     | 0        |
| Aksel     | Mean  | 169   | 3.97| 0.88| 28.69| 744 | 85.1| 6.7 | 35.6| 6.6   | 6.7 | 78.8| 9.1    | 6       | 0.09     |
|           | S.D.  | 5     | 0.1 | 0.01| 0.33| 46  | 0.9 | 0.6 | 0.5 | 0.4   | 0.1 | 0.0 | 2      | 0.02    | 0        |
|           | CV %  | 2.7   | 2.5 | 1.2 | 1.2 | 6.1 | 1   | 9.1 | 1.3 | 5.7   | 0.9 | 0   | 24.1   | 16.4    | 0        |
| BA-308    | Mean  | 163   | 4.89| 0.93| 30.98| 657 | 85.1| 6.3 | 35.2| 5.8   | 7.5 | 77  | 8.8    | 22      | 0.30     |
|           | S.D.  | 5     | 0.17| 0.01| 0.24| 29  | 0.7 | 0.3 | 1.7 | 0.7   | 0.1 | 0.1 | 0.1    | 0.01    | 0        |
|           | CV %  | 3.2   | 3.5 | 0.6 | 0.8 | 4.5 | 0.8 | 5.1 | 4.7 | 12.2  | 0.8 | 0.1 | 1.3    | 4.5     | 1.9      |
| Carmen    | Mean  | 144   | 4.92| 0.92| 27.92| 643 | 84.1| 7   | 32.6| 6.4   | 6.9 | 76.8| 8.6    | 5       | 0.13     |
|           | S.D.  | 7     | 0.04| 0   | 0.25| 114 | 1.2 | 0.7 | 0.5 | 0.4   | 0.2 | 0.1 | 0.4    | 0.07    | 1        |
|           | CV %  | 4.6   | 0.8 | 0   | 0.9 | 17.8| 1.5 | 9.4 | 1.4 | 6.2   | 3.4 | 1.3 | 4.2    | 21.7    | 54.3     |
| Celia     | Mean  | 174   | 3.31| 0.85| 28.41| 526 | 85.1| 6.3 | 35.9| 6.2   | 80.6| 8.5 | 10     | 0.27    | 2        |
|           | S.D.  | 10    | 0.1 | 0.01| 0.98| 20  | 0.6 | 0.3 | 2.5 | 0.5   | 0   | 0.1 | 0.1    | 0.01    | 2        |
|           | CV %  | 3.1   | 0.7 | 3.4 | 3.9 | 0.7 | 4   | 7   | 8.8 | 0     | 0   | 0.1 | 10     | 2.1     | 24.7     |
| Flora     | Mean  | 149   | 3.89| 0.86| 27.97| 625 | 84.1| 7.2 | 30.5| 6.8   | 6.6 | 78.4| 8.6    | 11      | 0.18     |
|           | S.D.  | 12    | 0.2 | 0.01| 0.87| 56  | 1.2 | 0.4 | 1.1 | 0.5   | 0   | 0.3 | 0.3    | 0.06    | 1        |
|           | CV %  | 8     | 5   | 0.7 | 3.1 | 9   | 1.4 | 5.7 | 3.5 | 7.8   | 0   | 0.3 | 2.9    | 60.3    | 35.9     |
| Stoneville-| Mean | 144   | 4.63| 0.9 | 28.85| 621 | 84.2| 6.9 | 31  | 6.6   | 7.6 | 76.1| 8.5    | 16      | 0.33     |
| 453       | S.D.  | 8.9   | 8.7 | 1.1 | 2.6 | 5   | 1.1 | 5.1 | 3.7 | 6.3   | 0.8 | 0.2 | 0.7    | 1       | 0.01     |
|           | CV %  | 8.9   | 8.7 | 1.1 | 2.6 | 5   | 1.1 | 5.1 | 3.7 | 6.3   | 0.8 | 0.2 | 0.7    | 1       | 0.01     |
Figure 6: WAXD traces of a) undyed cotton fibers and b) dyed cotton fibers

Table 2
X-ray diffraction data of undyed and dyed cotton fibers

| Fiber         | Peak position (2θ) (°) | d-Spacing (Å) | FWHM (β) (rad) | Crystal size (t_c) (Å) |
|---------------|------------------------|---------------|----------------|-----------------------|
|               | Undyed | Dyed | Undyed | Dyed | Undyed | Dyed | Undyed | Dyed |
| Adana-98      | 22.6684 | 22.7706 | 3.9227 | 3.9054 | 0.2362 | 0.6298 | 339.2255 | 127.2458 |
| Aksel         | 22.8493 | 22.5964 | 3.8921 | 3.9351 | 0.7085 | 0.3936 | 113.1270 | 203.5442 |
| BA-308        | 22.6212 | 22.6212 | 3.9308 | 3.9308 | 0.3936 | 0.3936 | 203.5530 | 203.5530 |
| Carmen        | 22.7398 | 22.8136 | 3.9106 | 3.8981 | 0.4723 | 0.2362 | 169.6699 | 339.3119 |
| Celia         | 22.8768 | 22.8490 | 3.8875 | 3.8921 | 0.3149 | 0.3149 | 254.5392 | 254.5267 |
| Flora         | 22.4668 | 22.5700 | 3.9575 | 3.9363 | 0.1968 | 0.3149 | 406.9966 | 254.4023 |
| Stoneville-453| 22.6334 | 22.8895 | 3.9287 | 3.8853 | 0.3149 | 0.2362 | 254.4305 | 339.3573 |

Wide angle X-ray diffraction (WAXD) patterns for undyed and dyed cotton fiber samples are given in Figure 6. The values of maximum 2θ peak positions, d-spacings, FWHM (β) and crystal sizes for undyed and dyed cotton fibers obtained from X-ray diffraction graphics are given in Table 2. The characteristic diffraction peaks of 002 planes for all the raw and dyed cotton fibers were obtained from the wide angle X-ray diffraction patterns. For both undyed and dyed cotton fibers, the maximum 20 peak values showed a shift in the X-ray diffraction patterns, but all these peaks were seen in the range of 22° and 23°. These results are compatible with the peak values of cellulose given in the literature. The changes of d-spacings for undyed and dyed cotton fibers are shown in Figure 7. After dyeing process, it was shown that the d-spacings of cotton fibers (Adana-98, Carmen, Flora and Stoneville-453) were generally decreased.
The full width at the half-height of the maximum peak (FWHM) ($\beta$) in the X-ray spectra shows the crystal perfection of fibers. When the peak ($\beta$) expands, the crystal perfection decreases.\textsuperscript{20-21,23} The change in the FWHM ($\beta$) values for undyed and dyed cotton fibers are shown in Figure 8. After the dyeing process, it was observed that the FWHM ($\beta$) values of Adana-98 and Flora increased, whereas those of Aksel, Carmen and Stoneville-453 decreased.

It is understood from the Scherrer equation that the crystal size varies inversely with FWHM ($\beta$). Crystal size also depends on the 2\(\theta\) value. When the crystal regularity increases, crystal size increases. The changes in the crystal sizes of undyed and dyed cotton fibers are shown in Figure 9. After the dyeing process, it may be noted that the crystal size decreased in the cotton fibers with large crystal size (Adana-98 and Flora), but it increased in the cotton fibers with small crystal size (Aksel, Carmen and Stoneville-453), compared to the respective crystal size of their undyed counterpart.

CONCLUSION

The aim of the present work was to understand the changes in the inner structure of cotton fibers induced by dyeing processes. The results of the wide angle X-ray diffraction analysis of cotton fibers showed that the inner structure parameters of cotton fibers are altered after dyeing. It was found that d-spacings, FWHM ($\beta$) and crystal sizes of cotton fibers were affected by the dyeing process. It was shown that the d-spacings of cotton fibers (Adana-98, Carmen, Flora and Stoneville-453) generally decreased, while the FWHM ($\beta$) values increased for some types of fibers (Adana-98 and Flora), but decreased for others (Aksel, Carmen and Stoneville-453). The crystal size of cotton fibers decreased in cotton fibers with large crystal size (Adana-98 and Flora), but increased in cotton fibers with small crystal size (Aksel, Carmen and Stoneville-453).

ACKNOWLEDGEMENTS: This paper is part of the MSc thesis entitled “Comparison of properties of some cotton fibers used in Turkey under the effect of dyeing”. The authors would like to extend their gratitude to Kahramanmarası Sütçü İmam University, BAP (Scientific Research Projects) for the funding support with grant number 2012/3-3YLS.

REFERENCES

1. J. W. S. Hearle, in “Cotton Science and Technology”, edited by S. Gordon and Y. L. Shieh,
Textile Institute CRC Press, Woodhead Publishing Limited, 2007, pp. 35-67

A. D. Broadbent, “Basic Principles of Textile Coloration”, Society of Dyers and Colourists, 2001

F. G. Goldwaith and J. D. Guthrie, in “Matthew’s Textile Fibers”, edited by H. R. Mauersberger, Wiley Interscience, 1954, pp. 219-256

A. Freitas and R. Mathews, “Viscose Fibres Production: An Assessment of Sustainability Issues”, 2017, https://waterfootprint.org/media/downloads/Viscose_fibres_Sustainability.pdf

Y. L. Hsieh, in “Cotton Science and Technology”, edited by S. Gordon and Y. L. Shieh, Textile Institute CRC Press, Woodhead Publishing Limited, 2007, pp. 3-34

D. Klemm, B. Philipp, T. Heinze, U. Heinze and W. Wagenknecht, “Comprehensive Cellulose Chemistry”, Vol. I: Fundamentals and Analytical Methods, Wiley-VCH Verlag GmbH, 1998

M. G. Uddin, Trends Green Chem., 2, 1 (2016), https://doi.org/10.21767/2471-9889.100011

Y. Xu, D. Chen, Z. Du, J. Li, Y. Wang et al., Carbohydr. Polym., 161, 99 (2017), https://doi.org/10.1016/j.carbpol.2016.12.071

Y. Nishiyama, J. Wood Sci., 55, 241 (2009), https://doi.org/10.1007/s10086-009-1029-1

A. Bafana, S. S. Devi and T. Chakrabarti, Environ. Rev., 19, 350 (2011), https://doi.org/10.1139/a11-018

F. M. D. Chequer, G. A. R. de Oliveira, E. R. A. Ferraz, J. C. Cardoso, M. V. B. Zanoni et al., in “Eco-Friendly Textile Dyeing and Finishing”, edited by M. Günyazı, IntechOpen, 2013, pp. 151-176, https://doi.org/10.5772/53659

D. King, in “Cotton Science and Technology”, edited by S. Gordon and Y. L. Shieh, Textile Institute CRC Press, Woodhead Publishing Limited, 2007, pp. 353-378

D. Shu, K. Fang, X. Liu, Y. Cai, X. Zhang et al., J. Clean Prod., 196, 935 (2018), https://doi.org/10.1016/j.jclepro.2018.06

B. K. Behera, P. K. Hari, S. Bansal and R. Singh, Indian J. Fib. Text. Res., 22, 84 (1997), http://nopr.niscair.res.in/bitstream/123456789/31991/1/IFTR%2022%282%29%2084-88.pdf

J. G. Koo, J. W. Park, S. K. An and Y. S. Koo, Text. Res. J., 73, 26 (2003), https://doi.org/10.1177/004051750307300105

A. R. Moghassem, Res. J. Text. Apparel, 12, 71 (2008), https://doi.org/10.1108/RJTA-12-01-2008-B009

S. H. Bahrami, P. Bajaj and K. Sen, J. Appl. Polym. Sci., 89, 1825 (2003), https://doi.org/10.1002/app.12275

P. Bajaj, T. V. Sreekumar and K. Sen, J. Appl. Polym. Sci., 86, 773 (2002), https://doi.org/10.1002/app.10973

G. I. Clark, in “Handbook of X–Rays” edited by F. K. Emmitt, McGraw-Hill Book Company, 1967, pp. 1-31

İ. Tiyek and F. Bozdoğan, Tekstil ve Konfeksiyon Dergisi, 18, 15 (2008), https://dergipark.org.tr/tr/download/article-file/218044

Y. Nishiyama, G. P. Johnson and A. D. French, Cellulose, 19, 319 (2012), https://doi.org/10.1007/s10570-012-9652-1

USTER Technologies, “USTER HVI Test Results”, in USTER Training Documents, 2002, http://csitc.org/sitecontent/RTCEA/internal_ea/02_RT_C_Content/022_Training/0222_Training_documents/02225_USTER/Application%20Manual/0222511_Test_results.pdf

K. Kimura, Y. Shimizu and J. Hayashi, “Cellulose and Cellulose Derivatives: Physico-Chemical Aspects and Industrial Applications”, edited by J. F. Kennedy, G. O. Phillips, P. A. Williams and L. Piculell, Woodhead Publishing Limited, 2009, pp. 85-92