NATIONAL TEXTILE CENTER
ProjectNo.: C-99 S04
Competency: Chemical Systems
Web site: http://www.ntcresearch.org/current/year8/C99-S04.htm

Fundamental Dye Diffusion and Surface Treatment of Fibers

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Introduction

The paper which follows this brief introduction has been recently submitted to Macromolecules and describes the main thrust of our project. In addition notable advances have been made in our modeling of dye diffusion in fibers [modeled and NMR diffusion coefficients for napthalene(dye) in hexane(polymer) found to agree] and in the LSCM observation of nylon-6,6 films dyed with C.I. Disperse Blue 3, which yield the diffusion, partition, and mass transfer convection coefficients of the dye in the nylon films. In addition, measurements of the reflectivties of fabrics and their individual fibers were performed after dyeing to various levels with disperse dyes. We are attempting to compare the fabric and fiber reflectivities as a function of depth of dyeing to learn about the relationship(s) between the visual appearance of dyed fabric and the visual properties of their constituent fibers.

LASER SCANNING CONFOCAL MICROSCOPY STUDY OF DYE DIFFUSION IN FIBERS

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ABSTRACT

The diffusion of fluorescein into nylon-66 fibers has been studied for the first time by Laser Scanning Confocal Microscopy(LSCM). LSCM makes it possible to non-invasively obtain high resolution three-dimensional images of the spatial distribution of fluoresce in fibers dyed for various times. Integration over the dye distribution yields the total amount of dye in the fiber, which is found to be in close agreement with that determined by UV-VIS spectrophotometry after dissolving the fibers. Thus, the diffusion coefficients determined non-invasively by LSCM(6.9x10 -11 cm**2 /s) and the destructive traditional means(7.8+1.9x10-11 cm**2 /s) also agree. The LSCM method has several significant advantages. Among these are its speed, non-destructive nature, and the ability to not only determine the total dye content of the fiber, but to image the dye distribution profile across the fiber diameter. This latter ability is demonstrated to be important to understanding the visual appearance of dyed fibers and fabrics. Two fibers, one ring-dyed and one uniformly dyed, each with the same over all dye content, show remarkably different shades of color. The ring-dyed fiber evidences a much deeper shade, an observation confirmed by the reflectivities measured for each fiber, which were in the ratio ring-dyed/uniformly dyed = 2/1. LSCM observation of dyed fibers

provides us not only with a means to measure the dye diffusion coefficient in the fiber, but also the time-dependent, three-dimensional distribution of dye as well.

INTRODUCTION

The appearance of certain kinds of defects in fabrics has been a problem for many years, in particular, the appearance of streaks. Streakiness results from a small absolute variation of lightness and is an objectionable feature for human observers. The amazing fact, however, is that the variation in lightness that cause streaks are hardly measurable by instruments. McGregor et al. [1], observed that extremely low variations in luminance of randomly varying parallel stripes (an oversimplified model for a fabric) can cause objectionable streaky appearance (Figure 1). Such low variations in reality could be caused by a number of factors which include, variations of the dye concentration in the fiber, spatial distribution of the dye in the fiber, shape of the fiber cross-section, the diameter of the fiber, spectral shifts of the dye due to the physical environment it finds itself in, and other factors related to the human visual system.

Studies of dye diffusion have been carried out in the past with the hope that some understanding can be gained about the appearance of defects. However, many of the methods are destructive techniques, and are ill suited for obtaining the spatial distribution of the dye molecules in a fiber. In a typical experiment, the fiber bundle is dyed under appropriate conditions and the amount of dye uptake as a function of time is measured. This can be easily accomplished by dissolving the fibers removed at regular time intervals, combined with the use of UV-Visible absorption measurements of dye concentration. This process is rather tedious and time consuming. Measurement of the concentration profile of the dye in the fiber using microspectrophotometry provides an alternative approach. However, there are two problems associated with this method: the difficulty of identifying the edge of the fiber and the possibility of dissolution of dye in the embedding materials. Both problems will introduce considerable error in the concentration profile and hence in the diffusion coefficient. Furthermore, these destructive techniques cannot be used in situations where fibers are under tension or during the process of forming internal or external cracks in the fiber. In conventional fiber dyeing measurements, information concerning the orientation of the dye molecules, the spectral characteristics of dye molecules or the spatial distribution of the dye in the fiber cannot be observed.

The appearance of a fiber depends primarily on how the fiber interacts with light. This interaction determines the amount of light that is reflected by the fiber. The shape of the fiber cross section can have a major impact on the appearance properties of the carpet or fabric made from the yarn [2,3] and non-round fibers are frequently used because of their effect on the appearance of the final product. Therefore it is important to have a three-dimensional image of the fiber for computations of reflectivity. The reflectivity of a of a fiber with a given shape can then be easily computed based on geometrical-optics, primarily by the use of ray tracing. It has been quite difficult to obtain a good three-dimensional image of the fiber when fibers have a shape other an infinite cylinder. Figure 2 shows the three-dimensional image obtained using a laser scanning confocal microscope (LSCM) of a trilobal nylon fiber that has been imaged using a fluorescent dye.

Despite the extensive use of LSCM in the biological sciences, its use in materials science is not nearly as extensive. LSCM has been used to image colloidal crystals in 3D [4-6] and to study the morphology of polymers [7], and phase separation of polymer blends [8]. The essential advantage of an LSCM is its ability to discriminate against unwanted out-of-focus light that limits a normal light microscope from obtaining a three dimensional image of a transparent object. This is accomplished by scanning a tightly focussed light source in a single plane that is thin compared to the sample thickness. The ability to discriminate against out-of-focus light is due to the fact that the detection system is confocal to the illumination, thereby only a single location in the specimen is imaged at any given time. Since the confocal aperture admits light only from the focal plane of interest, a very thin slice (x-y projection) can be obtained simply by scanning the beam in the x-y plane. Since each point in a focal (image) plane is examined individually, the in-plane or spatial resolution is enhanced, with achievement of a ~200nm resolution being typical, while the axial (z) resolution is around 500nm. The z-resolution is dependent on a number of parameters that include the size of the confocal aperture and the numerical aperture of the objective used for imaging. Since the images of the 2D (x-y image) sections are obtained in digital form, several successive optical sections can be used to construct a 3D image of the object.

Study of diffusion processes using an LSCM is still in its infancy. However, there have been a few studies devoted to the diffusion of tracer molecules in bio-membranes [9-15] using an LSCM. Florescence recovery after photobleaching type experiments were used to determine the mobility. In this study we report on the use of laser scanning confocal microscopy to the study of diffusion of tracer molecules into a solid (polymer) fiber. The results demonstrate that the spatial distribution of the dye is more important than the total amount of dye in the fiber with regard to the appearance of color and yield in the fiber. We are not only able to measure the diffusion coefficient of the dye, but also able to discern the orientation of the dye molecule[16], and of course, its spatial distribution, which prove to be very important in the perception of color.

EXPERIMENTAL

Nylon 66 fibers were dyed with fluorescein (0.1g/l, pH 6) in an infinite dyebath at 95°C. The concentration of fluorescein in the fiber was determined by the measurement of the absorbance of the formic acid solutions of the dyed fibers with an UV spectrophotometer. Fluorescein is a commonly used dye with maximum excitation at 490 nm and maximum emission at 515 nm. The fibers were imaged by a Leica DMRBE LSCM equipped with 488 nm laser line from an Argon ion laser and a 40 x NA 1.25 oil objective. The images were quantified and analyzed into fluorescent intensity profiles by using Leica TCS NT software. In order to minimize the aberrations that degrade the image, the refractive index of the object needs to be matched closely with that of the immersion oil for the objective and mounting medium for the specimen. Since the fiber is an anisotropic object, immersion oil that matches at least one of the refractive indices of the fiber was used [17].

RESULTS AND DISCUSSION

The process of fiber dyeing can be considered to occur in three stages: the diffusion of dye molecules from the solution to the surface of a fiber, the adsorption of the dye molecules on the surface, which is followed by the diffusion of the dye to the fiber center. Of the three stages, diffusion of dye molecules inside the fiber is the rate determining step, therefore making the study of dye diffusion in fibers of fundamental importance and the determination of dye diffusion coefficients essential. One of the most common methods to study dye diffusion is to perform an infinite dyebath dyeing in a very well stirred dyebath, in which the dye concentration is a constant. By determining the amount of dye uptake at given intervals of time, the diffusion coefficient can be calculated from Hill's solution of Fick's second law of diffusion, and can be written as [18]

$$\frac{C_t}{C_\infty} = 1 - A\,e^{-BK} - E\,e^{-FK} - G\,e^{-HK} \cdots\cdots$$

where C_t is the dye concentration at time t, C_∞ is the dye concentration at the equilibrium state, A, B, E, etc., are known numerical constants, and $K = Dt/r^2$, with D as the diffusion coefficient and r as the radius of the fiber. The diffusion coefficient D can be calculated from Hill's solution if the ratio of C_t/C_∞ is obtained. Traditionally C_t and C_∞ are determined individually from the absorbance of the solutions of dissolved fibers removed from the dyebath at times t and ∞.

In the fiber dyeing process, the amount of dye molecules transferred from the dyebath solution into the fiber is a function of dyeing time. As shown in Figure 3, the dye concentration in the fiber increased quickly at the beginning of dyeing and gradually reached equilibrium. The concentrations of fluorescein in the fibers were determined by measuring the absorbencies of the dissolved fibers in formic acid using an UV-VIS spectrophotometer. The average dye concentrations in the fibers were 0.28 g/kg, 0.55 g/kg, 1.1 g/kg and 1.4 g/kg after the fibers were dyed for 4 minutes, 16 minutes, 64 minutes and 256 minutes respectively. After the fiber was dyed for about 200 minutes, the dye concentration in the fiber became saturated and reached the equilibrium of dyeing. Therefore, C_∞ can be obtained and the diffusion coefficient can be calculated from Hill's solution of the diffusion equation. The diffusion coefficient was found to be $(7.8 \pm 1.9) \times 10^{-11}$ cm^2/s.

Conventional study of dye diffusion determines the total amount of dye uptake or the average dye concentration in the fiber without details of the dye diffusion process, such as the local dye concentration or the spatial distribution of dye molecules in the fiber and their changes during the dyeing process. This process is also tedious, time consuming and unable to provide the spatial distribution of dye in the fiber. In this work, we provide an elegant alternative method to study dye diffusion in fibers by using an LSCM. In this method, the spatial distribution of dye molecules in fibers and the diffusion coefficient of the dye can be quickly determined. To our knowledge this is the first report of using a LSCM to study dye diffusion in polymeric fibers.

The most significant advantage of LSCM is the ability of optical sectioning. By using an LSCM, the optical cross-section of a fiber can be easily obtained and so to the dye spatial distribution in the fiber if the fluorescent intensity is considered linearly proportional to the fluorescein concentration in the fiber. Figure 4 shows dye spatial distribution in fibers during the dyeing process. At the beginning of dyeing, the fluorescent intensity is higher near the fiber surface and becomes uniform only when dyeing reaches equilibrium. The linear relationship between the integrated fluorescent intensity and the concentration of fluorescein in the fiber is demonstrated in Figure 5. When the dye concentration in the fiber is lower than 5 g/kg, the total integrated fluorescent intensity is linearly proportional to the concentration of fluorescein in the fiber. In the experiments reported herein, the maximum dye concentration was 1.4 g/kg, thus providing data in the linear region of Figure 5. In addition, care was taken to keep the intensity of the illuminating laser below the saturation threshold of fluorescein. When the integrated fluorescent intensity is linearly proportional to dye concentration in the fiber, the ratio of concentrations C_t/C_∞ will be equal to the ratio of integrated fluorescent intensities, which can be obtained from the total integrated area of the fluorescent intensity profiles. Therefore, the concentration ratio C_t/C_∞ was obtained from the fluorescent intensity profiles of the fibers dyed for 4 minutes and 256 minutes (Figure 5), and a diffusion coefficient of 6.9×10^{-11} cm^2/s is calculated from Hill's solution. This result is in close agreement with the measurements $(7.8 \pm 1.9) \times 10^{-11}$ cm^2/s from the conventional method, thus demonstrating the validity and the value of the approach presented here.

The diffusion coefficient measured by the conventional method is based on yarn, which consists of a number of individual fibers. The rate of dye diffusion can be different between the individual fibers and that may contribute to the streakiness of textile fabrics. The diffusion coefficients measured by LSCM are based on the individual nylon fibers, however, they are in close agreement with the diffusion coefficients measured from the nylon yarn. Therefore, the rate of dye diffusion is unlikely a major factor to influence the streakiness.

It has been reported that ring-dyed fibers have higher color yield and appear deeper in shade than the homogeneously dyed fibers with the same overall dye concentration [19-21]. This indicates that the dye spatial distribution in the fiber can cause differences in color. We obtained two pieces of nylon yarns, both dyed with fluorescein and having the same total dye concentration, but the appearance is different in color, one has higher color yield than the other. The reflectance measured from the single fibers by a microspectrophotometer is shown in Figure 7, and LSCM images of cross section of these two fibers are shown in Figure 8. The fiber with the higher reflectance has the ring-dyed spatial distribution and the fiber with lower reflectance has the uniformly dyed spatial distribution. The uniformly-dyed fiber was obtained by placing the ring-dyed fiber in a blank dye bath containing no dye at 95 C for 24 hours. Measurements of refractive index, birefringence, and orientation distribution of dye molecules and polymer chains in each fiber indicated no significant difference between them, and no fluorescence spectral shift for the dye was found either[16]. This suggests that the color difference between the ring-dyed and uniformly dyed fibers, with the same total dye concentration in the fiber, is unlikely caused by variations in the physical properties or morphologies of the fibers. Instead, the spatial distribution of dye molecules in these fibers is the apparent reason for their different color yields and possibly a cause of streakiness in textile fabrics.

CONCLUSIONS

We have applied LSCM as a new nondestructive method to study dye diffusion behavior in fibers. This technique is simple and quick. It is able to provide high resolution images of the fiber cross-section, quantitative measurement of the diffusion coefficient and 3D images of the dye distribution inside the fiber. The diffusion coefficient of fluorescein in nylon 66 fiber measured by LSCM agreed with the result from the conventional method. We have provided further evidence that spatial distribution of dye molecules in the fiber can cause differences in the color of textile fabrics even if the fibers have the same dye concentration.

ACKNOWLEDGEMENTS

We are grateful for the assistance provided by Prof. Nina Allen at NC State and Dr. Carl Chiulli of the Polaroid Corporation. The financial support of this work was provided by the National Textile Center (Dept. of Commerce).

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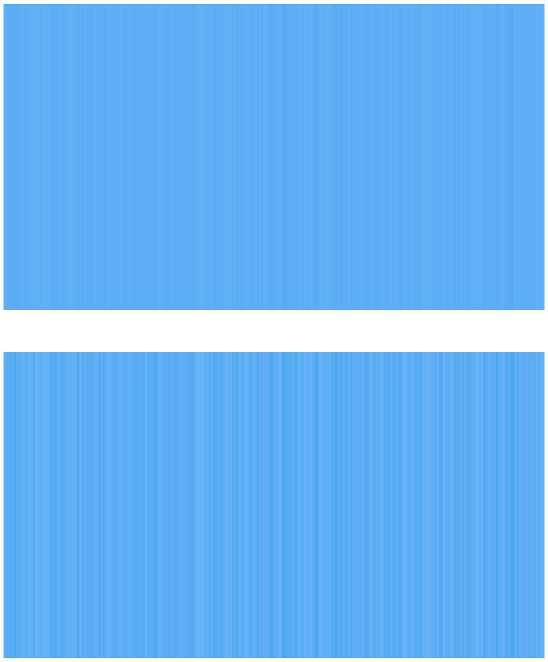


Figure 1. Demonstration of streakiness in textile fabrics. Top: reflectance variation is 0.7%. Bottom: reflectance variation is 2.1%. The appearance of streaks is due to small variation in the reflectance, which can be affected by a variety of factors.

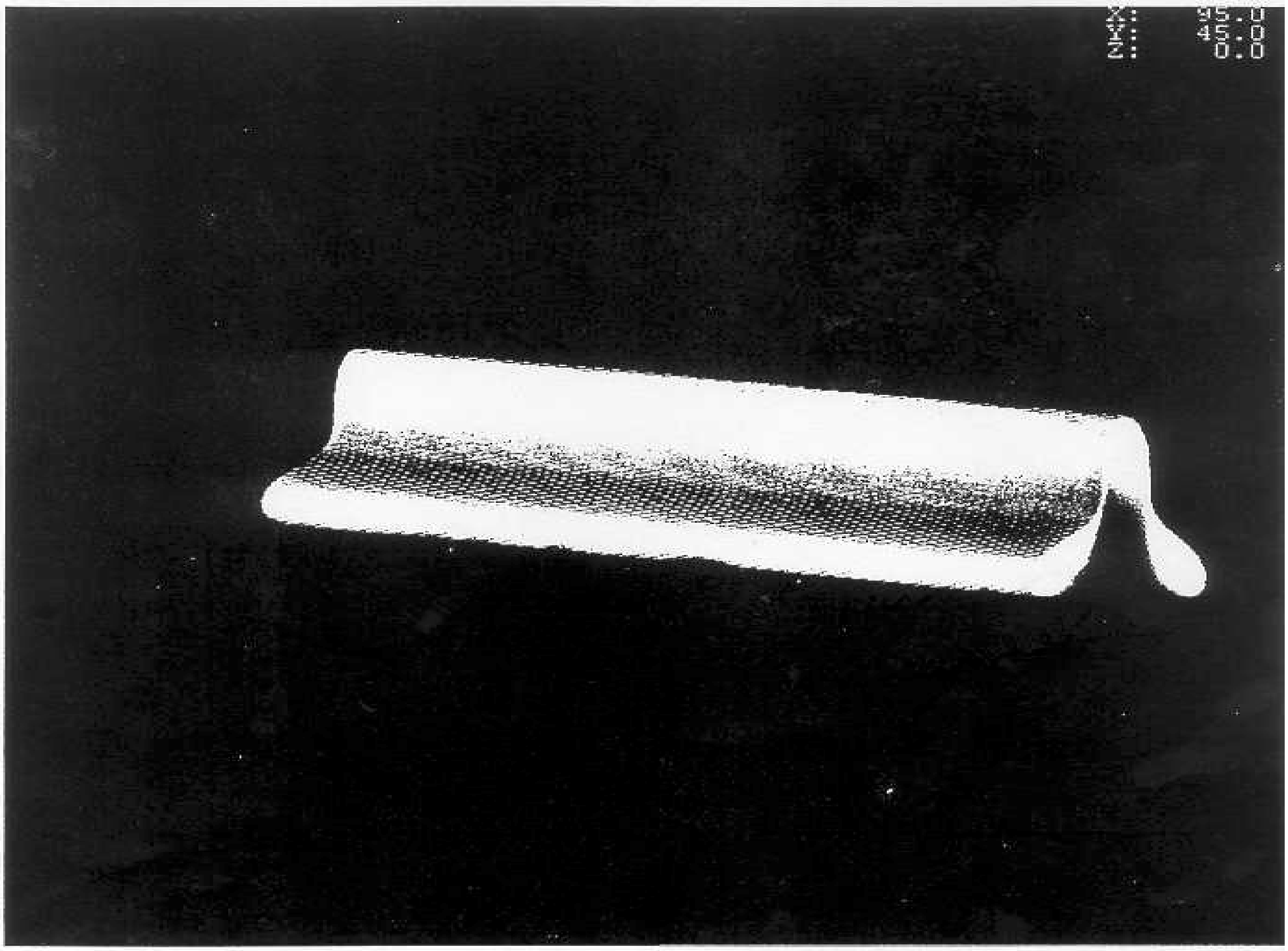


Figure 2. Three-dimensional LSCM image of a triloble nylon 66 fiber

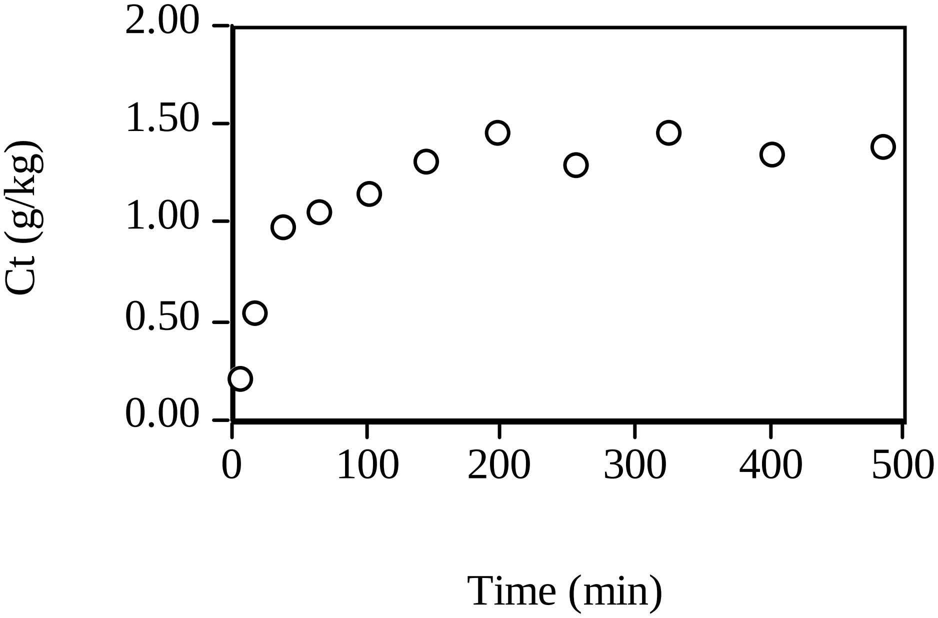


Figure 3. Plot of dye concentration in the fiber as a function of the time of dyeing. Nylon 66 fiber dyed with fluorescein in an infinite dyebath at pH 6, 95°C and dye concentrations in the dyebath was 0.1 g/l.

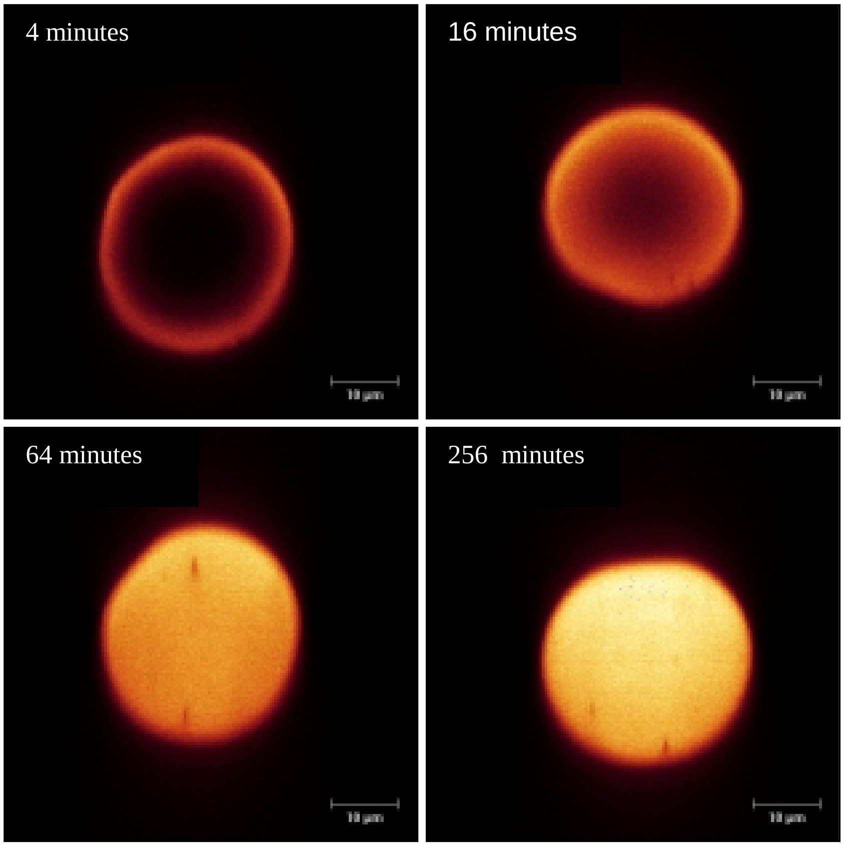


Figure 4. Images of fiber cross sections. The average diameter of the fiber is 30 µm. Nylon 66 fiber was dyed with fluorescein in an infinite dyebath for: 4, 16, 64 and 256 minutes. The dyebath was pH 6, 95°C and the dye concentration was 0.1 g/l.

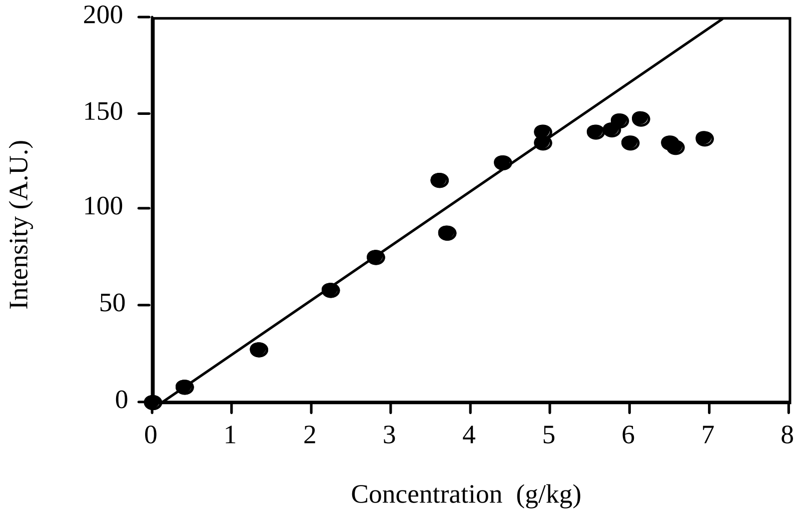
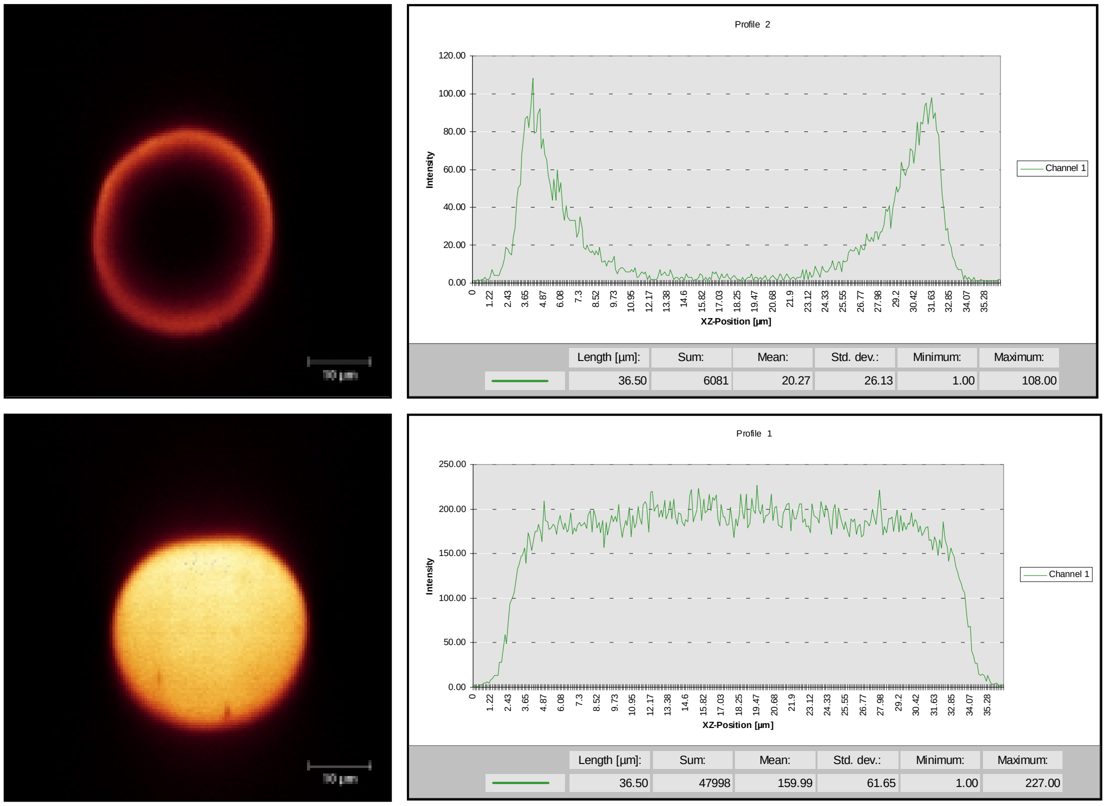


Figure 5. Plot of fluorescence intensity (arbitrary unit) as a function of fluorescein concentration in the fiber (g/kg). Nylon 66 fiber was dyed with fluorescein. Fluorescence intensity is linearly proportional to the fluorescein concentration in the fiber when the concentration is lower than 5 g/kg.



	Length [µm]:	Sum:	Mean:	Std. dev.:	Minimum:	Maximum:
―	36.50	6081	20.27	26.13	1.00	108.00

	Length [µm]:	Sum:	Mean:	Std. dev.:	Minimum:	Maximum:
―	36.50	47998	159.99	61.65	1.00	227.00

Figure 6. Top: image of fiber cross section and the fluorescence intensity across the fiber diameter when fiber dyed for 4 minutes. Bottom: image of fiber cross section and the fluorescence intensity across the fiber diameter when fiber dyed for 256 minutes. Nylon 66 fiber was dyed in an infinite dyebath at pH6 and 95°C. The dyebath concentration was 0.1g/l.

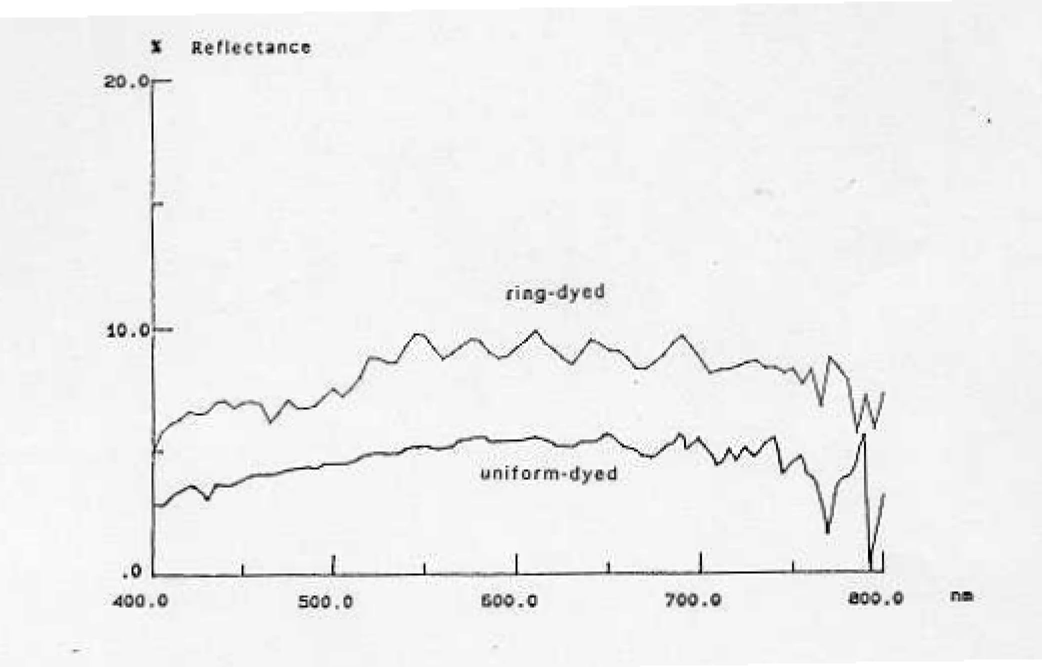
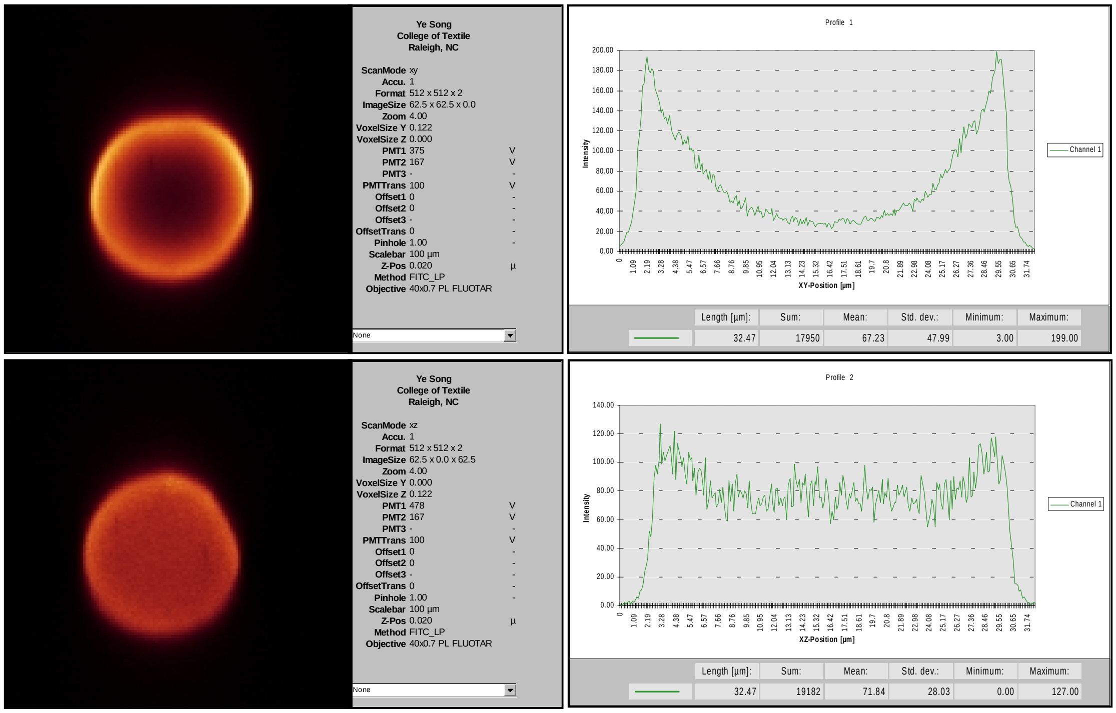


Figure 7. Measurement of reflectance from nylon 66 single fibers dyed with fluorescein. The ring-dyed fiber has higher reflectance than the uniformly dyed fiber with the same concentration in the fiber.



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ScanMode xy
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Zoom 4.00
VoxelSize Y 0.122
VoxelSize Z 0.000
PMT1 375 V
PMT2 167 V
PMT3 - -
PMTTrans 100 V
Offset1 0 -
Offset2 0 -
Offset3 - -
OffsetTrans 0 -
Pinhole 1.00 -
Scalebar 100 µm
Z-Pos 0.020 µ
Method FITC_LP
Objective 40x0.7 PL FLUOTAR

	Length [µm]:	Sum:	Mean:	Std. dev.:	Minimum:	Maximum:
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ScanMode xz
Accu. 1
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PMT3 - -
PMTTrans 100 V
Offset1 0 -
Offset2 0 -
Offset3 - -
OffsetTrans 0 -
Pinhole 1.00 -
Scalebar 100 µm
Z-Pos 0.020 µ
Method FITC_LP
Objective 40x0.7 PL FLUOTAR

	Length [µm]:	Sum:	Mean:	Std. dev.:	Minimum:	Maximum:
——	32.47	19182	71.84	28.03	0.00	127.00

Figure 8. Images of fiber cross sections and fluorescence intensity profiles across fiber diameter for ring-dyed (top) and uniformly dyed (bottom) fibers. Both fibers have the same total dye concentration. The ring-dyed fiber appeared darker than the uniformly dyed fiber.