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# A novel scCO2 dyeing strategy for superior coloration of UHMWPE fiber

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A B S T R A C T

Ultra-high-molecular-weight-polyethylene (UHMWPE) fibers have the highest stiffness-to-weight ratio of any available material, including metals. However, their applicability in consumer products is surprisingly limited. One reason for this is the inability to readily dye UHMWPE fibers, i.e. the fibers are only available in clear or black (carbon particle filled). Attempts to color UHMWPE fibers have only achieved limited dye uptake due to the high crystalline content of drawn UHMWPE fibers. In this study, we demonstrate that high dye uptake and high color intensity are possible in drawn UHMWPE via scCO2 dyeing of the as-spun fibers prior to drawing. The as-spun fibers are demonstrated to be drawn via standard methods into dyed high-performance fibers. Comparison of color intensity is made with UHMWPE fibers dyed after drawing and standard PET fibers. Mechanical properties are measured during the drawing process to demonstrate that the presence of dye does not reduce the drawability or the mechanical properties of the fibers.

Highlights

- A novel $scCO_2$ dyeing method of UHMWPE fiber is presented with superior dye uptake to traditional methods.
- The method utilizes as-spun fiber to increase dye uptake into amorphous domains of the fiber prior to drawing.
- A microscopic color correction technique is validated and used to determine color in a single fiber before and after drawing.
- The color fastness experiments show that the dye is not easily released from the fiber.
- Mechanical testing suggests that the presence of dye does not affect the modulus development with draw ratio.

## 1. Introduction

Ultra high molecular weight polyethylene (UHMWPE) is a widely used performance plastic because of its superior strength and low weight-to-modulus ratio[**?** ]. With a higher specific modulus and strength than steel, spider silk, and aramid fibers (Kevlar), UHMWPE fibers are finding uses in various industrial fields requiring strong tensile properties, e.g., body armor[**?** ], polymer composites[**?** ], ropes, fishing lines/commercial fishing nets [**?** ], parachutes and balloon cords[**?** ], tethers used in space and medical devices [**?** ]. There is a growing market for use of UHMWPE fibers in textile materials such as shoes, sportswear, and other consumer goods. One issue limiting the use of UHMWPE fibers in commercial textile products is the lack of availability of different colors. It is generally considered that UHMWPE fibers cannot be dyed using conventional dyeing systems due to extreme hydrophobicity and high crystallinity (>85%)[**? ?** ].

Two solutions have been proposed in the literature to color UHMWPE with varying degrees of success, including (1) infusing organic dyes into the stretched polyethylene [**? ?** ], (2) including particles, such as carbon black prior to spinning the fiber [**?** ], and (3) coloration of UHMWPE using a paint coating on the surface of the UHMWPE after fibers after surface modification [**? ?** ]. Method (2) is practised but has a disadvantage because of the potential loss of properties with particulate additives included into the polymer and the need for cleaning the extrusion equipment and nozzles between color additives. Method (3) has limited life because the surface coloration is damaged with use.

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The success of Method (1) is argued to strongly depend on the shape and structure of the dye molecule being infused and the limited dye capacity within the highly oriented and crystalline structure of UHMWPE fibers. Method (1) is also limited by the color palette possible and the amount of dye that can be incorporated, which limits the depth of color and color intensity that can be achieved. For example, researchers have reported the success of dyeing polypropylene with "super" hydrophobic dyes having long alkyl substituents, such as alkyl modified anthraquinoid dyes[**?** ]. And previously, Jaehyuk et al. have shown that using supercritical carbon dioxide($scCO_2$) in the presence of co-solvent decalin improves the dye uptake in UHMWPE fabrics. However, this dyeing process caused a reduction in the mechanical properties of UHMWPE fabrics [**?** ].

In this work, we propose a novel method of dyeing UHMWPE after spinning, but before post-drawing. We demonstrate that superior coloration and thus the widespread adoption of UHMWPE fibers in textiles can be achieved by incorporating PE-philic (molecules that like PE) dyes in the early stages of fiber formation using $scCO_2$ to trap the dye in the amorphous region of the PE. The fiber is subsequently drawn to achieve extreme tensile properties that are unaf-

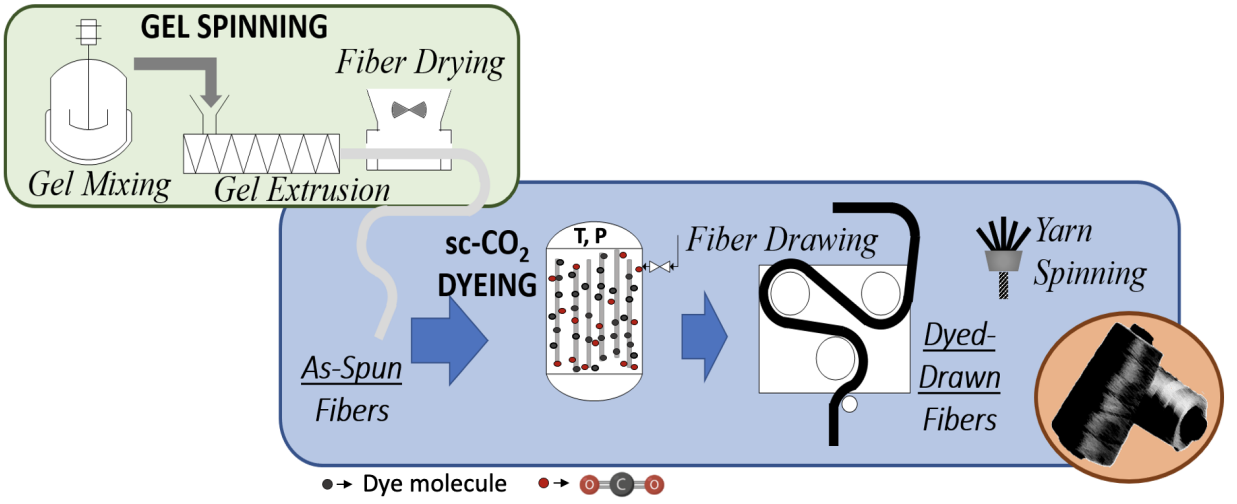


**Fig. 1**: Schematic of the proposed method of production of dark-colored UHMWPE yarns.

fected by the presence of dye 1. The process is significantly safer and environmentally friendly than traditional textile dyeing produces huge amounts of wastewater and has the added benefit of component recyclability, cost-effectiveness, decreased processing times, and preservation of material integrity [**?** ]. Our results show that our dyeing process significantly increases the dye uptake compared to the method (1), allowing UHMWPE fibers to achieve the color of standard PET-dyed yarns.

## 2. Material and Methods

### 2.1. Preparation of UHMWPE Gel and Fiber spinning

99.5 wt% UHMWPE (3-6×$10^6$ g/mol Sigma Aldrich CAS9002-88-4, Batch) and 0.5 wt% 2,6-di-tert-butyl-p-cresol and 3,5-di-tert-butyl-4-hydroxy-hydrocinnamte (antioxidants) were dissolved in decahydronaphthalene (Sigma Aldrich CAS911-17-8) and mixed in a 34 $cm^3$ stainless steel cylinder inside a rotary oven. The oven was held at 150 °C and rotated at 20 rpm for at least 20 hours. The sample was loaded into the temperature-controlled stainless steel hopper of a novel spinning apparatus [**?** ]. The spinning apparatus used a stainless steel piston with velocity control, i.e. flow-rate control. The range of flow rates was 10–45 $mm^3/s$ and the temperature was 120°C. The gel was extruded through a nylon nozzle (Plastic Process Equipment, RTEG334118) with a 3.2 mm diameter opening and drawn via a take-up motor at specified windup rates. The final diameters of the as-spun fibers were 600-700 $\mu$m. The as-spun fibers were air-dried for 5-6 hours and placed in a vacuum oven to dry at room temperature for a minimum of 8 hours. The dried fibers were used without further processing in the supercritical dyeing setup described below. The fibers were deemed to be dry and no effort was made to quantify residual solvent in the fiber. More details of the spinning and drying

| Dye Name | Color Index | Sample Result Color |
|---|---|---|
| Solvent Red 27 | C.I.26125 | Red |
| Solvent Green 3 | C.I.61565 | Green |
| Solvent Violet 13 | C.I.60725 | Blue |
| Disperse Brown 22 | C.I.11133 | Brown |
| Foron Black | N/A | Black |

**Table 1**
List of the dye used in this paper.

process can be found in Henry et al. [**?** ] Also used in this work are commercial stretched UHMWPE fibers from Honeywell sold under the trade name Spectra fibers. Spectra 900 uncolored UHMWPE fibers were used for dyeing work.

## 2.2. Fiber Dyeing

The dyeing process for the UHMWPE fibers consisted of $scCO_2$ as the solvent and a series of dyes referred to as disperse dyes. The disperse dyes are typically used in dyeing polyester yarns and fabrics, and they are soluble in scCO2.[**?** ] The dyeing of the fibers is done batch-wise in a heated high-pressure vessel. First, the UHMWPE or other textile fibers or yarns along with the dye/s are placed in the pressure vessel. The chamber is filled with $CO_2$ and brought to the target temperature and pressure. The $CO_2$ is circulated within the vessel to ensure dye dissolution, contact of the dye solution with the yarns/fibers/fabrics, and uniform coloration. The dyeing was done at 120 °C and a pressure of 3750 psig for 60 minutes, after which the vessel is depressurized and the dyed fibers removed. Polyester yarn and fabric were dyed in the same $scCO_2$ vessel as UHMWPE fibers to establish the color characteristics achieved with a specific dye at pressure and temperature. The dyed polyester served as the reference or "standard color" in this evaluation. In some cases, polyester and UHMWPE fibers were dyed during the same run, to determine if there are differences in the color characteristics caused by the material structure and morphology. The materials were dyed with the following dyes in this work:

## 2.3. Color Measurements

Before we could assess the viability and success of the supercritical dyeing process, a method of quantifying the dye concentration in fibers was needed. Spectroscopic methods were attempted with little success, and therefore a color method was tested and used to correlate dye uptake with dyeing conditions. Significant effort was dedicated to the development of a color measurement and calibration code that allowed us to consistently measure the real color of the fibers for each dye and fiber characteristics, i.e. fiber diameter. Typical polyester fiber or filament diameters used in textiles can range from 10 to 30 microns in diameter.

The color characteristics of the dyed fabric samples were measured using a Datacolor 600 color measurement system, which is widely used in the textile industry. The measurements were done using D65/10 lighting conditions within the colorimeter. The equipment measures the L*, a*, b*, C*, and H* color profiles for yarns and fabrics. The color measurement system can also be calibrated with specific dyes and dye uptakes in the yarns/fabrics to provide quantitative color measurements and for color matching.

However, for single fiber measurements, the Datacolor 600 could not be used due to the limit of the detector. Instead, a microscope setup was developed for single-fiber imaging and color analysis. The setup included a BH200-MR Series Metallurgical Microscope with 10x magnification coupled with a Touptek photonics FMA0500 camera to obtain pictures of each fiber and yarn. The light source was a PHILIPS TYPE 5761 30W low voltage halogen lamp. Color analysis was optimized and applied to correct the color obtained by this method.

## 2.4. Color analysis

There are several challenges with a microscope setup for accurate color analysis of single fibers. For example, the illuminating condition of the microscope setup leads to non uniform intensity across the sample surface, compared to the uniform lighting condition of the Datacolor 600. Furthermore, the microscope setup uses a halogen lamp source

while the Datacolor 600 uses a standard daylight illuminant. Lastly, the optical elements in the microscope will influence the color observed and therefore must be calibrated for accurate color measurements to be achieved. In general, the microscope is capable of resolving defects and slight variations in color patterns, which requires an averaging technique for comparison to the single color measurement of the Datacolor 600. It is known that K/S measurements for thin fibers have a few limitations. For smaller diameter fibers, such as microfibers the light focused on these fibers has less surface area to interact with compared to higher diameter ones. This causes much of the light to scatter resulting in weak spectral curves. Thus, the absorbance data for colored microfibers will not provide the same information about the chemical dye(s) typical with larger-diameter colored fibers. For these reasons, we choose to use a color correction procedure to obtain the corrected L a and b parameters instead of the K/S of the microfibers. [**?** ] Previously, Charriere et al. developed a color calibration method for a macroscale RGB camera-mounted microscope setup. [**?** ] This method extracted relative color information from a strong, distorted image taking into account the non-uniformity and surface texture of the image.

Following their work, we developed a method to study and characterize fiber colors on a highly magnified microscopic scale. Using a similar calibration routine to Charriere et al., microscopic images of a standard color chart, X-Rite ColorChecker®Classic Mini Model #MSCCMN-RET (MSCCMN), were taken using the microscope setup and corrected for in CIELAB space. More specifically, an image of each color patch was taken using the microscope and TOUPCAM RGB camera. The raw average color was extracted from each patch for processing. First the average patch color was corrected for white balance, and then gamma correction. The gamma correction requires shifting the white-balanced images via correlations between the camera values and the true color values of the MSCCMN standard. Similar to Charriere et al.'s method, a correlation between the raw $L$ values and the true $L$ values of the MSCCMN was achieved via a second-order polynomial fit. A similar correlation was achieved between the $C$ values of the CIELAB space using a second-order polynomial fit. Both correlations are used for the initial processing of the microscope images, before applying the matrix calibration correction. Finally, an optimization routine was performed to develop a matrix transformation of the white balance, gamma corrected and shifted raw images to the final color-corrected images.

The CIELAB color space is shown in figure 2b. The L*-axis represents the lightness, where L*=100 denotes white, while L*=0 denotes black and intermediate values shades of grey. Chromatic colors are described by using the green to red axis, i.e.a*, and the blue to the yellow axis, i.e b*. A measured color is represented by a color point (L*, a*, b*) in the color space, where L*, a*, and b* are the color coordinates.

Figure 2 shows each process of the color correction algorithm for each patch of the MSCCMN reference standard. The first row shows the average raw image color of each patch. The second row shows the result of the white balance correction. The third row shows the Gamma Correction via correlations of $L$ and $C$ discussed above. Finally, the colors are corrected via the optimized shifting matrix on row four. The fifth row shows the MSCCMN standard color for comparison. We observe excellent agreement between the corrected microscope colors and the reference standard colors for the first 18 columns. Columns 12-24 represent the grey scale range. In this range, the correction routine had issues with matching the MSCCMN reference standard. We were unable to achieve better agreement using different lighting and focus of the microscope setup, and thus argue that these deviations may arise due to the contrast limits of the camera.

## 2.5. Validating the color correction analysis method

Although the color correction routine was developed using the MSCCMN standard, it is important to validate the correction routine using additional materials. For this purpose, We compare the corrected color of PET-dyed fabric swatches with the Datacolor colorimeter 600.

And the software setting is set to the same condition when taking all the microscopic images, including the photos for the color checker, the fabrics, and also the fibers.

The microscopic images of the fabric swatch were then color-corrected using the same color-correcting algorithm. The average colors' $L*$, $a*$ and $b*$ values of the color-corrected images were then compared with the $L*$, $a*$, and $b*$ value reading from the Datacolor colorimeter 600. The color difference, specifically $E^*_{94}$, between these two color methods was used to quantify the validity of our microscope setup. The average $\Delta E^*_{94}$ between our microscope method and the Datacolor colorimeter are 3.63, 3.42, and 0.38 for red, violet, and green dyes, respectively.[**?** ] Typically a color error of two is considered to be indistinguishable from the human eye. Although not within this limit, the very small $E^*_{94}$ values demonstrated that our microscope color correction method is capable of achieving very similar

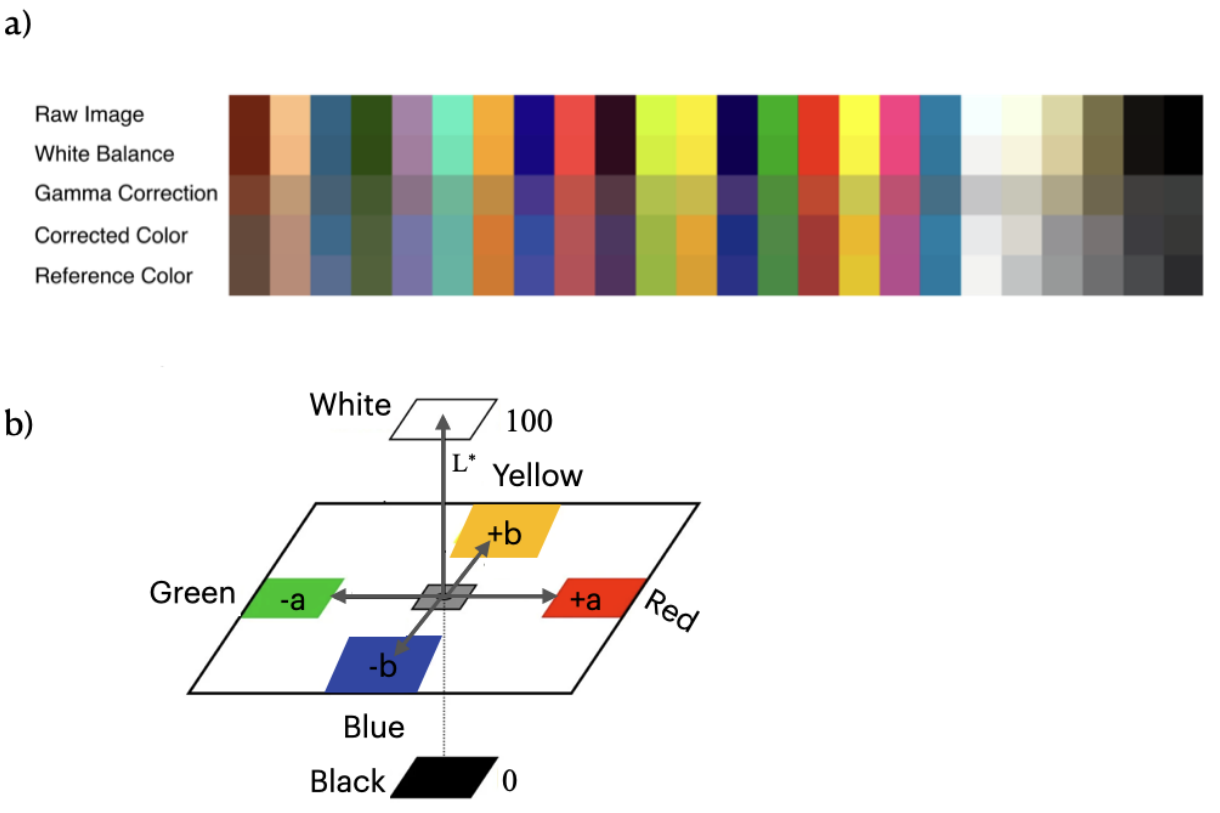


**Fig. 2**: a) Raw image, white Balance, gamma correction, corrected color and reference color of the color correction procedure using a default 24 colors map, b) Scheme of the CIELAB 3d color space (Modified from [**?** ]).

colors to that measured by the Datacolor colorimeter. Note that ideally, we would have used the colorimeter for all specimens. Unfortunately, however, the colorimeter requires much larger specimens than a single-colored fiber. Thus, the microscope color correction method is considered a suitable alternative that is certainly justifiable in comparisons within itself, but also relatively close to a commercial colorimeter output.

## 2.6. Fastness test

An alcohol wipe test and water washing test were performed to evaluate the color fastness of the dyed UHMWPE fiber. In the alcohol wipe test, alcohol wipes saturated with 70% isopropyl alcohol (COVIDIEN TM Webcol TM Alcohol Prep) were used for this experiment. A 5 cm length fiber was secured on one end. The alcohol wipe was rubbed 50 times along the fiber length in a downward direction. The wipe was checked for any transfer of dye to the wipe surface. Pictures were taken using the microscope protocol discussed above before and after the test. The color fastness of the fibers was evaluated by comparing the change in CIE-Lab values measured from the microscopy images.

The water washing test was developed based on standard method ISO 105 C06:2010[**?** ]. Note that the standard specifies the use of detergents for this test. However, for our tests, we followed a detergent free protocol that has been presented in the literature [**?** ]. The test consisted of heating 500 ml DI water (Millipore Q) in a beaker to 50°C using a standard hot plate. A white non-woven cloth was cut into 10 cm by 4 cm strips, and a 5 cm length dyed fiber sample was sewn onto the white non-woven cloth. The fibers were additionally secured onto the non-woven cloth using a hot glue gun. T The sample was submerged into the water bath and stirred at 500 RPM for 30 min. Pictures were taken using the microscope protocol discussed above before and after the test. The color fastness of the fibers was evaluated

by comparing the change in CIE-Lab values measured from the microscopy images.

### 2.7. Fiber Drawing and Mechanical Properties

The drawing and mechanical testing of UHMWPE fibers were conducted using a VADER 1000 (Rheofilamnet ApS) adapted for solid mechanical testing, see Henry et al. for details [**?** ]. Both methods involved stretching fiber samples at a constant velocity between two custom clamps. The drawing of the samples was performed by stretching the dyed UHMWPE fibers at 120°C, 15°C below melting [**?** ]. Each drawing stage was performed by stretching the fiber at constant velocity (0.5mm/s) from 5 mm initial length to 100 mm, which is a lateral draw ratio, $DR_L = L_f/L_0 = 20$, where $L_f$ is the final length and $L_0$ is the initial gauge length. Since slippage and non-uniform deformation can occur during drawing, the radial draw ratio, defined as $DR_D = D_0/D_f$, is a more accurate representation of the fiber deformation during drawing. The initial, $D_0$, and the final, $D_f$ diameters were measured before and after drawing, respectively, using the microscope setup discussed above. Between each drawing stage, the fibers were left to cool down for 10 min before being handled. Additional drawing stages were performed by cutting a uniform section of drawn fiber, reclamping to an initial 5mm gap, and stretching again.[**?** ]

The mechanical testing of the fibers was performed at room temperature, 10 minutes after drawing, via unloading experiments. The cooled fiber samples after drawing were unloaded via a downward velocity of the top capstan. The decreasing force and displacement were measured, and the modulus was calculated using a calibrated stress-strain method. Strain calibration was performed using the "Elastic Deformation of Known Material" method reported by Kalidindi et. al [**?** ] to accurately correct the machine compliance. The strain calibration method was validated using three fibers with known Modulus (Nichrome, Copper, and Stainless Steel). An example of strain correction using Nichrome is shown in Figure S1.

## 3. Results and Discussion

### 3.1. Dye uptake

#### *3.1.1. Comparison of UHMWPE to PET fibers*

Figure 3,5, and 7 shows the color correction results of the dyed commercial UHMWPE spectra fiber, PET fibers, and as-spun fibers with different draw ratios. All fibers in the same color group were dyed in the same batch. The average $LAB$ color values of dyed fibers are shown in each image, along with the respective fiber diameters.

Figure 3(a),(b), and (c) shows that the color uptake of the three fibers is very vivid. Note that of all the dyes, the red dye had the highest uptake in the drawn UHMWPE Spectra fibers. The PET yarn and fibers show smaller $L$ values and larger $a$ and $b$ values than the commercial UHMWPE yarn. This means that the color of the PET fibers is more concentrated and vivid than the commercial UHMWPE fibers. Interestingly, the color of the undrawn as-spun fiber was unable to be measured as the color was too saturated for the microscope setup. This means that the as-spun fiber achieved considerable dye uptake. As the as-spun fiber was drawn, the color of the fiber remained very dark compared to the PET and Spectra samples. This signifies that more dye was present in the dyed as-spun fiber compared to the other two fibers. Figure 4 shows the effect of drawing on the measured fiber color for the dyed as-spun fiber. For the two draw stages, we observe very little color change with decreasing diameter. Furthermore, the color of the fibers after the drawing is very similar to the PET fibers, and slightly darker red than the dyed Spectra fiber.

Figure 5shows the fibers colored using a green dye. The striking difference between red and green dyed spectra fibers is that the green dyed spectra fibers show almost no color, i.e. a very high $L$ value. Overall, the spectra fibers can be concluded to have minimal if no dye uptake for the green dye. On the other hand, the color of the dyed PET and as-spun fibers are much more vibrant. Note that the as-spun fiber, as in the case of red dye, was too saturated in color to be measured with the microscope setup, hence the black appearance. However, as expected, the color of the dyed as-spun fiber became measurable with increasing draw stages. At the highest draw stage, the as-spun fiber shows a more vibrant blue than the PET fibers, suggesting a higher dye uptake. Note that the PET fibers show a slightly greenish tint in color, denoted by its smaller negative $b$ value, while the UHMWPE fibers show a much bluer tint, i.e. more negative $b$ value. This difference was not observed in the red dye tests. At this time, it is not clear why the UHMWPE and PET fiber colors differ so strongly using green dye. Figure 6 shows the effect of drawing on the $Lab$

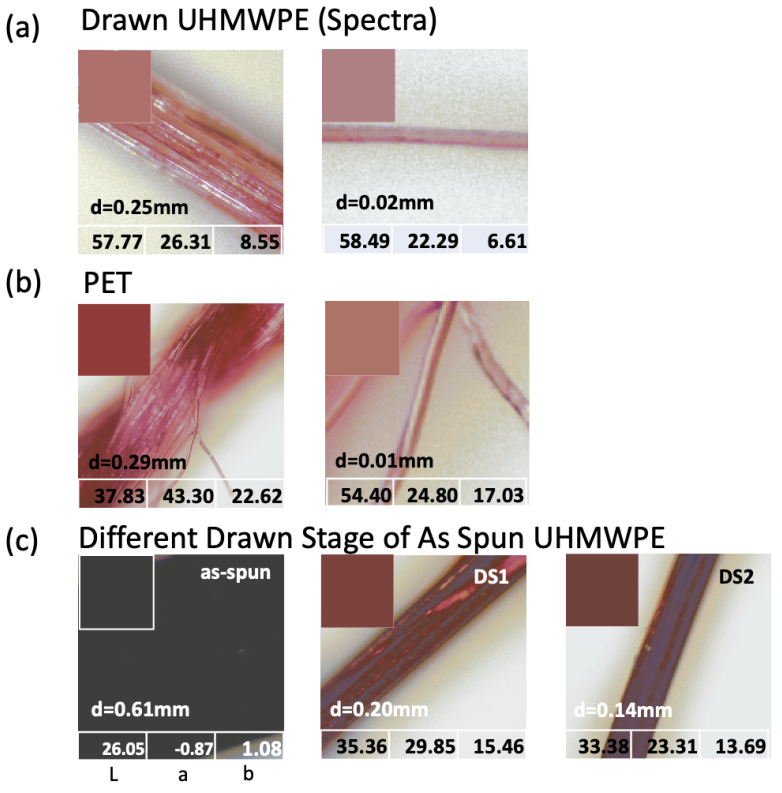


**Fig. 3**: Comparison of (a)spectra fiber, (b)PET fiber, and (c)as-spun fiber dyed with red dye.(c) showed dyed as-spun fiber in three different drawing stages.

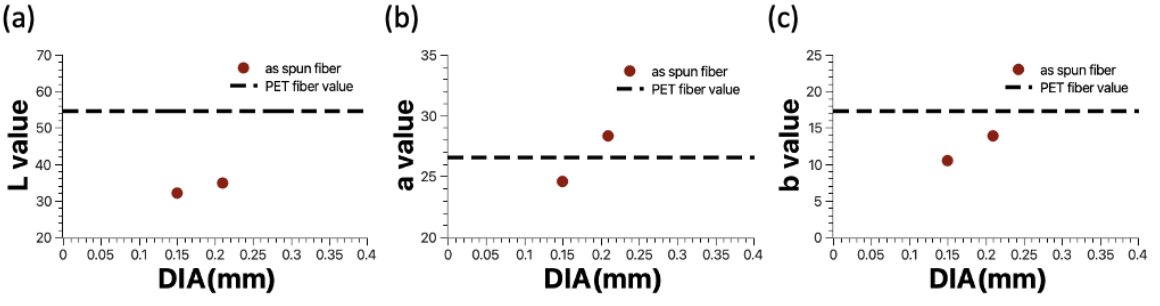


**Fig. 4**: Comparing the change of $L$, $a$, and $b$ values of the first and second drawing stages of the as-spun fiber dyed with red dye.

values for the green dyed as-spun fiber. We observe that the color is not strongly impacted by the decrease in diameter, but due in fact approach to the values of the dyed PET fibers. This suggests a very similar dye uptake between PET and the dyed as-spun fiber, which are both markedly different from the dyed Spectra fiber.

Figure 7 shows the color results for all fibers dyed with the violet dye. The color of the violet spectra fiber is more vibrant than the green UHMWPE spectra fiber, but it is obviously less vivid than the red spectra fiber. Similar to the red and green fibers, the violet PET fiber also shows a smaller $L$ value than the commercial UHMWPE fibers, which indicates it also has a higher dye uptake than the commercial UHMWPE fibers. After several stages of drawing, the violet-dyed as-spun fiber went from an immeasurable dark color to a purplish blue. And as the drawing stages increased, the drawn as-spun fiber became lighter in color. At the highest draw stage (DS3), the as-spun fiber shows a similar color to the PET fibers, which indicates a similar color uptake. However, this fiber also shows a strong re-

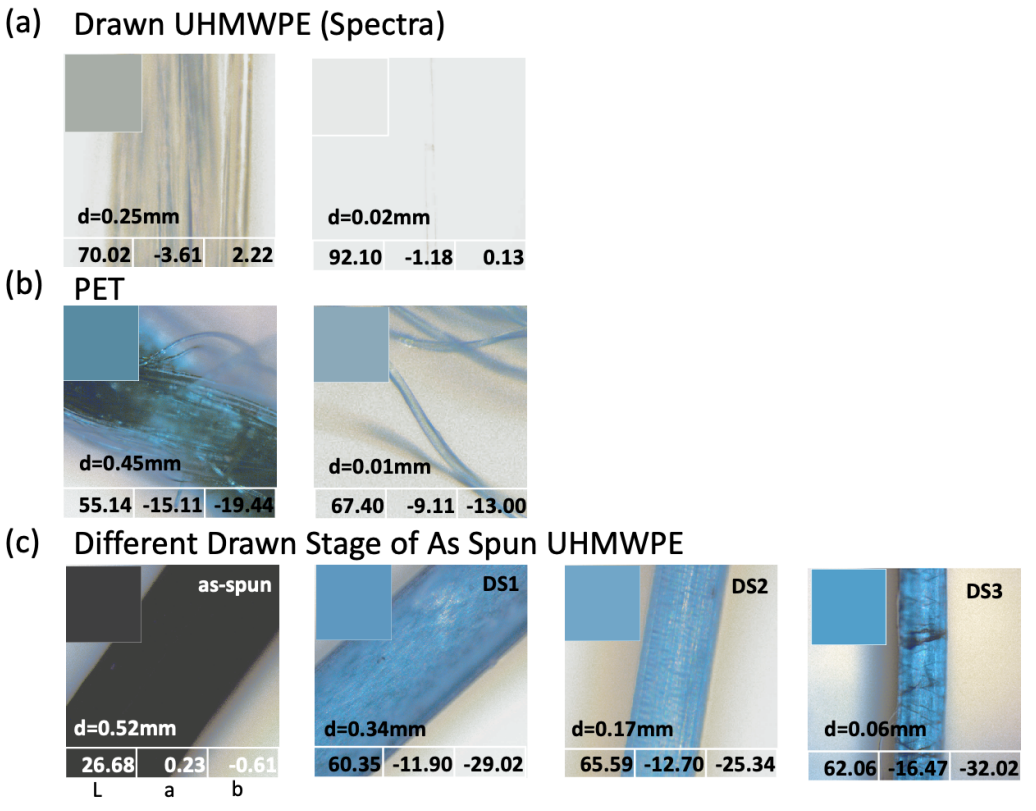


**Fig. 5**: Comparison of (a)spectra fiber, (b)PET fiber, and (c)as-spun fiber dyed with green dye.(c) showed dyed as-spun fiber in four different drawing stages

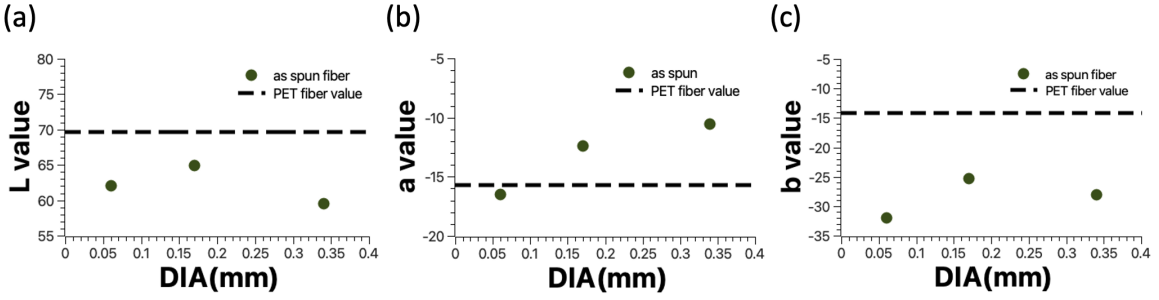


**Fig. 6**: Comparing the change of $L$, $a$, and $b$ value of the first and second drawing stages of the as-spun fiber dyed with green dye.

flection, which means the actual color of the fiber might be more vibrant than measured with the microscope setup. Figure 8 shows the effect of drawing on the $Lab$ values of the dyed as-spun fiber. We observe, similar to the green dye, that as the diameter of the fiber decreases, the more the $Lab$ values approach that of the dyed PET fibers. This again suggests that the dye uptake of PET and as-spun UHMWPE fibers are similar, and much more concentrated than the dyed Spectra fiber.

One explanation for the significant differences observed between dyed Spectra and dyed as-spun UHMWPE fiber is their differences in crystallinity. Previously, Jaehyuk et al. have shown that there is a correlation between the dye uptake and the degree of crystallinity of UHMWPE fabrics dyed in $scCO_2$.[**?** ] Fibers with a higher degree of amorphous

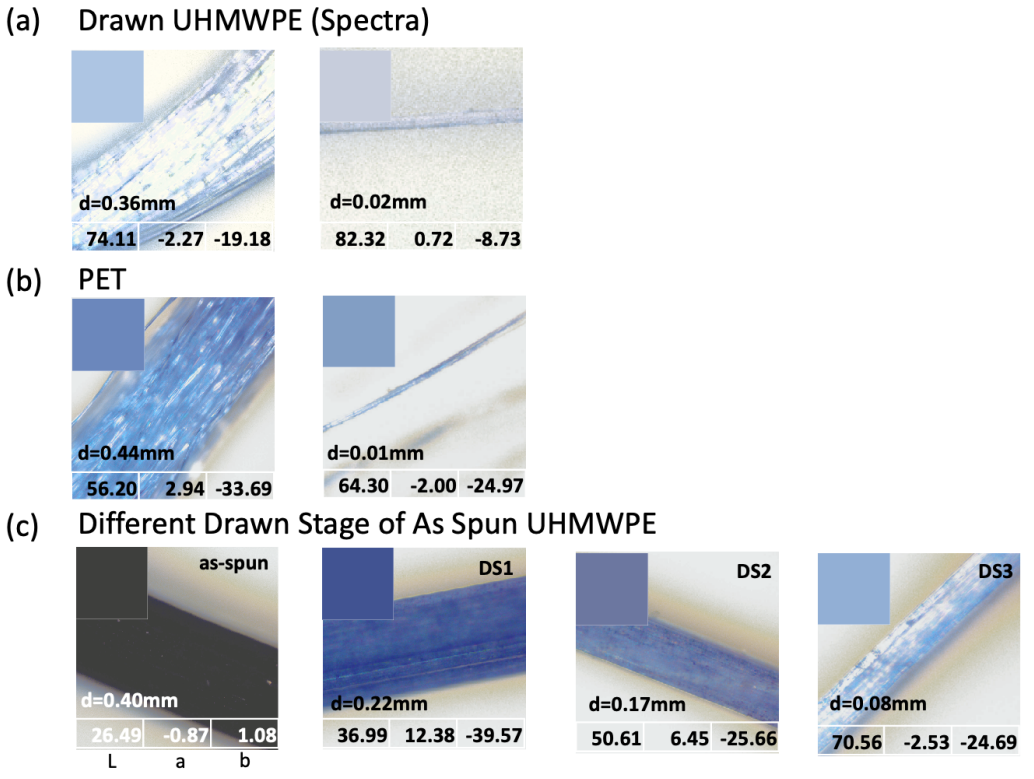


**Fig. 7**: Comparison of (a)spectra fiber, (b)PET fiber, and (c)as-spun fiber dyed with violet dye.(c) showed the dyed as-spun fiber in four different drawing stages

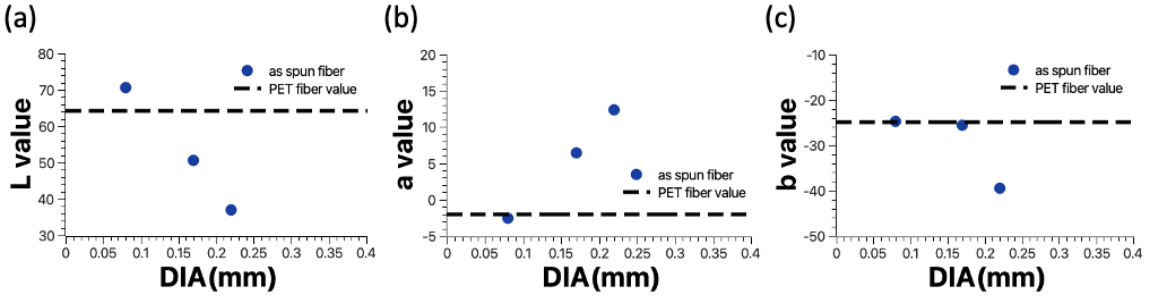


**Fig. 8**: Comparing the change of $L$, $a$, and $b$ value of the first and second drawing stages of the as-spun fiber dyed with violet dye

content showed higher levels of dye uptake, see scheme in figure 9.

In this study, the Honeywell Spectra s-900 has a reported crystallinity greater than 92 %[**?** ], the PET fibers have a typical crystallininty between 30-50% [**? ?** ], and the as-spun UHMWPE fibers have a reported crystallinity between 74-79%.[**?** ] Thus if the only important parameter was the degree of crystallinity, then we would expect the PET fibers to have the highest dye uptake, most intense dye color, and the Spectra fiber to have the lowest, i.e. least intense color. While it is clear that the PET fiber has more dye uptake than Spectra fibers, in some cases, the dye uptake in the as-spun UHMWPE fiber seems to be equal or slightly greater than that of PET, e.g. in the case of the red and green dyes. This suggests that 21-26% amorphous content is sufficient to achieve dye saturation in the fiber. However, one must be cautious here since the drawn as-spun fiber and PET fibers are not being compared at the same diameter. It is possible that with more drawing, the dyed as-spun fiber would show less color than the PET fiber. This is supported by

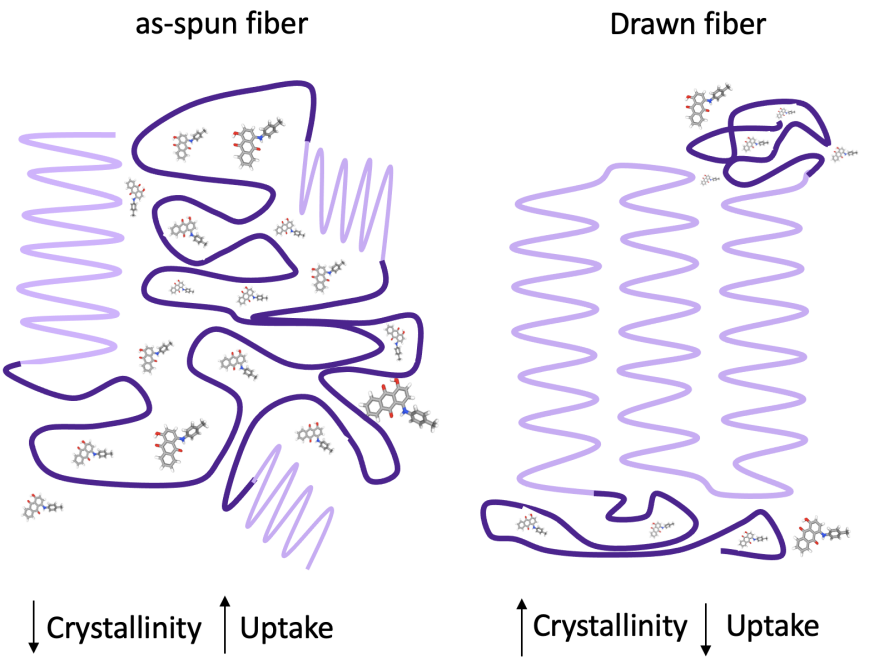


**Fig. 9**: Scheme of difference between dye uptake by fibers with different crystallinity (as-spun and drawn fiber)

the trends in *Lab* with higher draw stages. Unfortunately, due to our experimental setup, the UHMWPE fibers could not be drawn below a diameter of 0.06 mm. Note that brown and black dyes were used to dye as-spun fiber, but the quantitative color analysis was not performed due to the limitation of our color correction methodology. We now ask whether the presence of the dye has any effect on the Mechanical properties of the drawn fibers.

### *3.1.2. Color Fastness*

The alcohol wipe test was performed on all DS1 dyed fiber specimens. Figure S4 shows images before and after the wipe test. In all cases, there is no significant change in fiber color, signifying close to maximum fastness (i.e. 5) using isopropanol for all dyed fiber specimens (typically ranked on a 1-5 scale, where 5 indicates no change). Note that there was no observable dye transferred to the alcohol wipe after testing for all three dyed fibers. Note that the fastness test is typically performed using grayscale images, however, we felt that the color image comparison is more informative.

The water-washing test was used to evaluate the color fastness after simulating daily washing. Figure 10 shows characteristic image of each DS1 fiber and the normalized distributions for the L, a, and b channels of the CIE-Lab coordinates for each fiber before and after washing. The distribution was normalized by dividing the intensities by the peak intensity, i.e. the peak intensity was normalized to unity. The normalized distributions were chosen, instead of an average CIE-Lab value, to more accurately represent the changes in fiber color after washing.

We observe from these results that all three fibers have very similar distributions before and after washing, with only subtle differences. For example, the red dye shows almost no change in L, a, and b distributions after the washing cycle. Using the grayscale intensity value determined from the Figure S5, there is less than a 1% change in grayscale intensity, signifying a fastness of 5. The green dye shows a slight shift in the L value of the fiber towards lighter color, signifying some loss of dye from the fiber. From the grayscale intensity results, the green dye shows a change of 13%, see Figure S5, signifying a fastness of 4. Lastly, the violet dye shows the largest shift in L value, signifying the largest loss of dye due to washing. Using the greyscale intensity results, we observe an overall intensity change of 38%, which

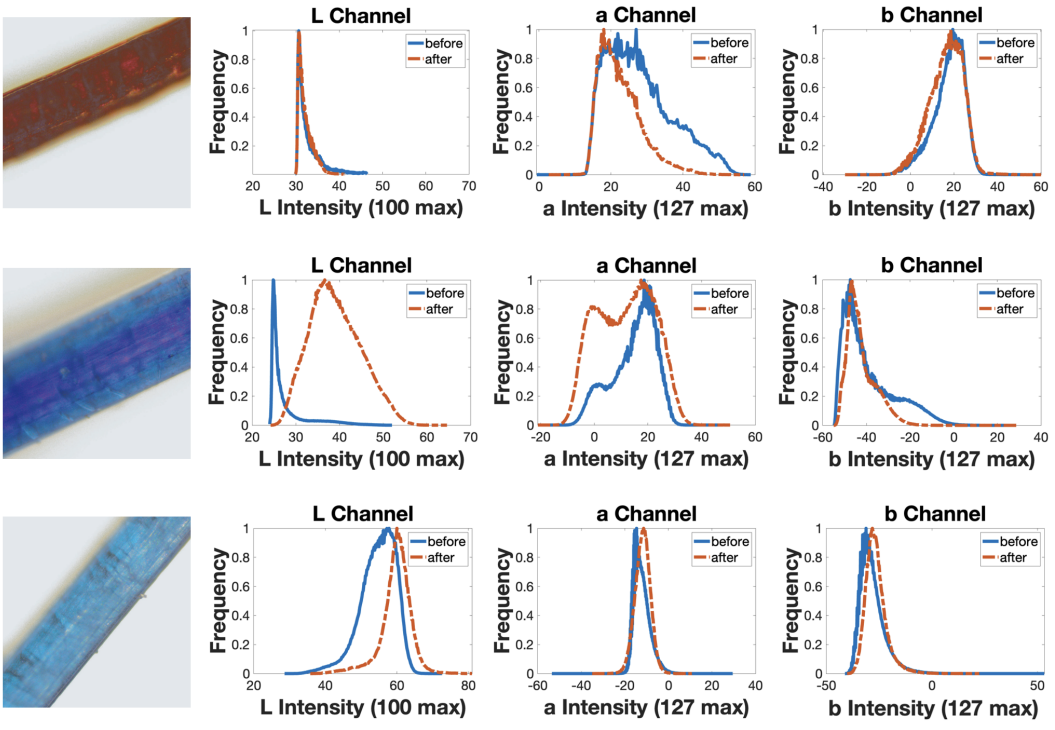


**Fig. 10**: Comparison of CIE-Lab distributions for all DS1 dyed fiber samples before and after the washing fastness test.

is noticeable to the naked eye and would constitute a fastness rating of 3. It is clear from these results that the dye was not restricted to the surface of the fibers, but rather was able to penetrate into the bulk. However, these results do indicate that the degree of fastness in UHMWPE dyed fibers is molecule specific. More work is needed to better understand the relationship between chemical structure and fastness rating.

## 3.2. Mechanical Properties

Figure 11 shows the measured Elastic modulus ($E$) of undyed, black, brown, green, and red fibers as a function of draw ratio ($DR_D = D_0/D(DSi)$), where $D_0$ is the as-spun diameter, and $DS(DSi)$ is the diameter measured at a given draw stage. The $E$ of the fibers were obtained by the equation below:

$$E = \frac{\tau}{\epsilon} = \frac{\Delta F L_0}{A \Delta L}, \tag{1}$$

where $\tau$ is the stress on the fiber, $\epsilon = \Delta L/L_0$ is the axial strain, $A$ is the cross sectional area of the fiber, and $\Delta L$ is the change in length of the fiber. Examples of the compliance-corrected load-displacement curves are presented in Figure S2.

As expected the elastic modulus increases with $DR_D$ for all colored fibers [**? ?** ], and is similar to the evolution of undyed (white) fibers. Note that the undyed (white) fibers are considered a control as they are produced with the same spinning setup and treatment as the dyed fibers. The Modulus of the dyed fibers was higher or comparable with the undyed samples, which confirms that the supercritical dyeing process does not prevent the UHMWPE straight chain crystal evolution during drawing. Fibers with diameters around 200 $\mu$m, i.e. $DR_D \approx 3-5$ had $10 < E < 40$ GPa depending on color. The brown fiber was drawn to $DR_D = 6$ or $D_f = 70$ $\mu$m and had a modulus $E \approx$80 GPa, which is close to the limit of commercially spun UHMWPE fibers. Spectra fibers have a diameter of $\approx 20$ $\mu$m and Modulus of $\approx 110$ GPa (Figure S2 a)). Interestingly, we can observe that at the same DR, Red, and Brown fibers have a higher modulus than the green, white, and black fibers for a given $DR_D$. The reason for this is the subject of an ongoing investigation. Overall we observe that the dyeing process has no adverse effect on the ability of as-spun fibers to be

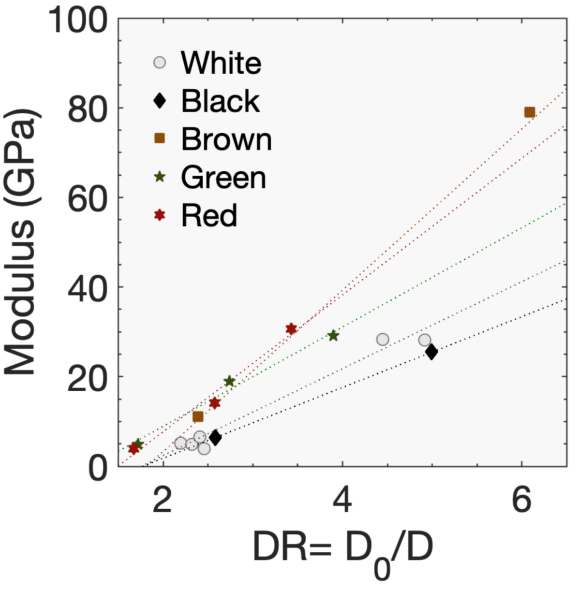


**Fig. 11**: Modulus as a function of draw ratio of white (undyed), black, brown, green, and red fibers.The dash lines in the figure are guides for the eyes.

drawn to high-modulus fibers.

## 4. Conclusions

In conclusion, we have shown that the colors of the post-drawn as-spun fibers are more vivid than the pre-drawn Spectra 900 fibers dyed under the same conditions. Indicating that dyeing the fiber prior to drawing is an effective method of achieving commercially relevant dye concentrations in UHMWPE fibers. Overall, the drawn UHMWPE as-spun fibers were able to achieve colors similar, if not more intense, to PET fibers that were dyed under the same conditions. These results are in agreement with previous studies, showing that effective dye uptake requires a certain degree of amorphous content in the fiber material. The data suggests that an amorphous content of approximately 70% is sufficient for effective dye uptake. Measurement of Elastic modulus for the dyed and undyed fibers show that neither the supercritical dyeing process nor the presence of dye molecules has any appreciable effect on the ability to draw as-spun fibers. Moreover, the color fastness tests have shown that the dyes penetrate into the fiber bulk, and all tested fibers were able to retain all their color with the alcohol wipe test. The wash test revealed that the retention of color during the washing depends on the molecular structure of the dye, with the red dye showing the highest fastness rating, and the violoet dye showing the lowest fastness rating. In conclusion, we demonstrate that the inclusion of a $scCO_2$ dyeing step between spinning and drawing is a fascile way to achieve deep vibrant colors in UHMWPE fibers that can be post-drawn to achieve the desired mechanical properties. The colors achieved are expected to resemble the colors that can be readily achieved with PET fibers. This method should allow for UHMWPE to be more readily used in commercial applications that require a range of colors. Especially applications that currently use PET fibers, but could benefit from UHMWPE fiber properties with the same color profile.

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**Conflicts of Interest**

All authors declare a conflict of interest. M.A. has a financial relationship with ECO2dye.