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EXAMINING THE EFFECTS OF ENVIRONMENTAL DEGRADATION ON THE OPTICAL PROPERTIES OF MANUFACTURED FIBERS OF NATURAL ORIGIN*

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ABSTRACT

Synthetic fibers derived from natural, biological resources are used frequently in textiles and clothing. These fibers include viscose rayon, azlon, and polylactic acid (PLA), among others. Little is known about the changes occurring in their optical and physical properties as an effect of moisture, sunlight exposure, and exposure to various temperatures. Such changes may become important when forensic examiners are comparing fibers suspected to be from the same source, but subjected to different environments. A two-year study was undertaken in order to document any changes these biologically derived polymers undergo as a result of such environmental conditions. Fabric swatches representing each fiber type were exposed to freshwater, saltwater, heat, cold, ultraviolet light, and composter conditions. Every eight weeks the swatches were subsampled and analyzed via polarized light microscopy. Morphology and optical properties were recorded, including refractive index, pleochroism, birefringence, extinction characteristics, and sign of elongation. Infrared spectra were collected every eight weeks. Solubility and melting point behavior were assessed every 6 months. Except for complete degradation, no significant changes were seen in the optical properties, infrared spectra, solubility, or melting points of any of the fibers in any of the environments for the duration of the experiment. However, morphological changes were observed in two PLA swatches and two viscose swatches exposed to UV light, as well as one azlon fabric submerged in either freshwater or saltwater. All viscose swatches in the composter and water environments eventually degraded away completely. These results indicate that forensic fiber comparison can reasonably be conducted on such fibers exposed to different environments, while highlighting possible explanations for some observed morphological differences.

Keywords: forensic science, criminalistics, fiber identification, fiber degradation, azlon, polylactic acid, viscose fiber, polarized light microscopy, Fourier transform infrared spectroscopy, melting point, solubility

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Naturally occurring polymers have been used in fiber manufacture for more than a century. In fact, the oldest commercially successful synthetic fiber is viscose rayon, made from cellulose, and first synthesized in the 1890s (1). Recently, due to improved manufacturing methods, inexpensive raw materials, and increased public awareness of environmental impact, other fibers from naturally derived biological polymers have become increasingly popular in textiles and clothing. Such fibers are referred to as Manufactured Fibers of Natural Origin, or MFNOs. Manufacturers tout them as being biodegradable, and a preferred alternative to persistent fibers such as nylon or polyester. Azlon is another MFNO using protein as the raw material, and polylactic acid (PLA) is an MFNO that starts with starch.

Because the polymer is naturally derived, we theorized that MFNOs are thus more likely to be affected by environmental conditions over time, and any changes in their optical and physical properties due to degradation may have consequences in the forensic laboratory. Forensic fiber examiners usually identify and compare fibers based on their infrared spectra, as well as optical properties such as shape, size, refractive index, birefringence, and extinction characteristics. Physical properties such as melting point and solubility may also be measured. However, because of the newness of some of these fibers, there is a paucity of research on the effect of environmental degradation. The nature of the degradation, as well as the degree of degradation, may become an issue to forensic scientists in several ways. For example, fibers presented as evidence may have spent time in unsatisfactory conditions. Clothing fibers remaining on a body that was dumped in a saltwater bog may undergo changes in their optical properties. When compared to fibers collected from a suspect's home (and thus kept in a less destructive environment), the fibers may be falsely excluded when their optical or physical properties no longer match. This research was undertaken in order to better understand the effects of such environmental processes on these fibers.

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Materials

Three types of MFNOs were evaluated in this project: viscose rayon, azlon, and polylactic acid (PLA). Most were items of clothing, though bolts of fabric were included as well. The fabrics were unwashed, unworn, and purchased online from consumer retailers. These items represented multiple manufacturers, and, according to label information or Registered Identification Numbers (RNs), originated from the United States, China, Mexico, and India. The fabrics were either composed entirely of the fiber of interest, or were blended with other fiber types. This was verified microscopically, since labels are not always correct. (Indeed, two items of apparel were improperly labeled: a scarf labeled “100% viscose” was actually 100% polyester, and a sweater labeled “100% Soy” was actually 100% viscose.) Different weaves and weights were used, and undyed, unpigmented fabrics were preferred, though some items were lightly colored. In addition, both delustered and bright fibers were represented.

Viscose Rayon Fabrics

Viscose rayon is typically made using cellulose from cotton linters or softwoods such as spruce or pine. The wood is pulped, and the cellulose is separated and purified. Then it is steeped in sodium hydroxide and dried, followed by mixing with carbon disulfide, and eventually extruded through a spinneret into a coagulating bath (1). The resulting fiber is used in a variety of consumer products, ranging from apparel to towels and bedding.

Five viscose clothing samples were selected for this project, as detailed in Table 1. Fiber content ranged from 100% viscose to 34% viscose, and blends included silk, nylon, polyester, cotton, and Spandex®.

Azlon Fabrics

As defined by the Federal Trade Commission (FTC) azlon fibers are comprised of any regenerated, naturally occurring protein (2). The proteins used are typically the byproducts of

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other manufacturing processes: casein (milk protein), zein (corn protein), or most commonly, soy protein. Azlons were first synthesized in the 1890s, but were rather brittle and too fragile in the presence of water to be of use as a textile fiber. In 1935, a stronger, more practical azlon was produced via treatment with formaldehyde or aluminum salts, creating cross-linkages between the proteins in the fiber. The fiber underwent large-scale production under the trade names of Aralac, Fibrolane, Lanital, Ardil, and Vicara, among others, and was commonly blended or felted with wool or rabbit hair. With the advent of the more durable polyesters and nylons in the 1960s, the production of most azlon fibers was discontinued (1). Currently, new production methods, including incorporating polyvinyl alcohol into the spinning solution (3), have resulted in modern azlons. Textiles may be 100% azlon or blended with cotton, silk, nylon, or wool. The fabric is promoted for its softness and is used in undergarments, shirts, and sweaters.

Five textiles containing between 40% and 98% azlon were sampled in this study (Table 1). Blends included cashmere, cotton, spandex, and “metallic” thread.

Polylactic Acid Fabrics

Polylactic acid (PLA) fibers were designated by the FTC as a new fiber type in 2002 (4, 5). It is derived from naturally occurring sugars and composed of at least 85% lactic acid ester units (2). Commercial production of PLA begins with starch (usually corn starch) as the raw material, which undergoes enzymatic hydrolysis for conversion into dextrose. The dextrose is fermented to produce lactic acid; after which It then undergoes a condensation reaction into the cyclic lactide. Heating the lactide in the presence of a tin catalyst (typically stannous octoate) allows for the ring-opening and subsequent polymerization of the polylactic acid (6). PLA is currently being mass-produced by companies in the United States (Natureworks, LLC) (4, 5), Japan (Kanebo) (6, 7), and China. PLA textile products include apparel, upholstery, and carpet fibers.

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Seven PLA textiles were analyzed in this study. Five contained 100% PLA, while the sixth was 70% PLA (blended with nylon and spandex) and the seventh was 37% PLA (blended with nylon, polyester, and spandex).

Fabric Swatches and Preparation

After the textiles were verified to contain the fiber of interest, they were photographed, and then cut into six 4x4” and one 3x3” swatches using a razor blade and a corresponding square of plastic as a guide. For exposure to UV light, the 3”x3” swatches were smaller than the others in order to fit on the bottom of a 20”x10”x12” fish tank. These swatches, as well as those placed in the freezer and control environments, had no further manipulation. Swatches destined for either of the two water environments were fitted with two sets of plastic snap-together grommets (Dritz, Spartanburg, SC) placed at diagonal corners. Nylon fishing line was then threaded through each grommet, one tied to a fishing bobber and the other tied to a sinker. Thus the swatches would be held suspended underwater. One grommet was attached near a corner of each swatch going into the oven, and a plastic-coated paper clip was slightly unbent and used to suspend the swatches from the oven rack. Swatches placed in the composter had one grommet attached near a corner, with nylon fishing line threaded through. The ends of the line were tied to magnetic clasps, such that the nylon “necklace” could be easily removed from the composter’s axle when required.

Environments

Six different environments were created in the lab: hot, cold, ultraviolet (UV) light, freshwater, saltwater, and composter. A seventh group was the control: swatches were placed in paper envelopes and stored at room temperature in a dark cabinet. To replicate a hot environment, a laboratory oven (model ED-23, Binder, Bohemia, NY) was kept at 70°C (158°F). This temperature was chosen based on studies showing that the interior of a automotive vehicle

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can easily approach that on warm, sunny days (8). A consumer-grade freezer (Frigidaire, Augusta, GA) served as the cold environment. A calibrated digital thermometer with a bottle sensor and cable (Control Company, Friendswood, TX) was used to monitor the temperature, which was maintained between minus (-) 25.0 °C and 6.4°C. Weekly readings of high and low temperatures were recorded. The ultraviolet light was meant to replicate light from the sun, and as such, the 20W fluorescent bulbs emitted ultraviolet light in the range of 315 – 400nm, 24 hours a day, seven days a week. Bulbs were installed in a grow light ballast and placed atop a dry 20x10x12" fish tank. Swatches were placed on the bottom of the tank, and flipped over every 8 weeks to ensure maximum UV exposure of all yarns in the swatch. Two 50-gallon fish tanks, one filled with freshwater, one with saltwater (average specific gravity of 1.023 g/cm^3, or approximately 3% salinity) were outfitted with filters and circulating pumps and maintained by a professional reef expert for the duration of the experiment. The water in both tanks was kept at a neutral pH. Filtering and circulating the water ensured microbes and/or algae did not build up excessively over time. Water was replaced as necessary. Although the temperature was not regulated, temperature readings from calibrated digital thermometers (Control Company, Friendswood, TX) were recorded on a weekly basis, with the maximum and minimum temperatures for the week. These temperatures ranged from 11.04 – 27.78°C for the freshwater tank, and 8.96 – 27.89°C for the saltwater tank. The composter was an outdoor tumbling bin, ("Back Porch" model) manufactured by ComposTumbler (Lancaster, PA). A PVC pipe was mounted inside as a central axle from which the fiber swatches were attached with nylon fishing line. Green and brown materials, such as grass clippings, fruit and vegetable waste, coffee grounds, egg shells, and dry brown leaves were added in an approximately 50:50 ratio several times per week. The composter drum was manually turned when new materials were added. Because this composter was situated outdoors in Chicago, during the winter months (November – April) it was inactive and the contents frozen. The composter's fibers

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were still analyzed for the sake of consistency, but data from these time periods are considered "paused." Thus, the fabrics were only exposed to composting activity for 13 months total: July – October 2012, May – October 2013, and May – July 2014.

Methods

Fibers were collected from each swatch for analysis every eight weeks during the two-year duration of the experiment. With 17 swatches (five each of viscose and azlon, seven of PLA) and six environments, this amounts to 102 total swatches to be analyzed every eight weeks. Because of the volume of samples, the fibers were first placed into the environments at staggered time periods: PLA on 02 July 2012, azlon two weeks later on 16 July 2012, and viscose two weeks after that on 30 July 2012. Thus measurements of the different fiber types were also offset by two weeks, allowing one week for analysis followed by a one-week break. Optical properties measured included those that are commonly performed during forensic fiber analysis: morphology, size, refractive index, birefringence, extinction, sign of elongation, and Fourier-Transform Infrared Microspectroscopy. Because of concerns with intra-sample variation, multiple fibers from each swatch were analyzed. In addition, solubility and melting point were assessed every six months.

Data was collected and verified by two research analysts independent of each other. Any discrepancies were reviewed in order to determine the cause, and the fiber was re-analyzed. Data, photomicrographs, and IR spectra were stored on a dedicated computer and backed up hourly.

In order to make the research findings applicable to forensic scientists, only analysis methods that are typically employed in a forensic laboratory were used in this study. Thus, physical properties often measured by fiber manufacturers, such as tenacity and moisture regain were not considered here. In a typical forensic laboratory, fiber evidence is first examined with the unaided eye and the stereomicroscope to assess length, crimp, color, luster,

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etc. Next, the fiber is mounted on a microscope slide and examined using the polarized light microscope (PLM). The PLM allows the forensic fiber examiner to measure optical properties, including refractive index, birefringence, and extinction. These measured properties may be compared to tables or flow charts (9) listing the optical properties of known fibers in order to identify the fiber type, and possibly the sub-type of fiber. In addition, morphological features may be assessed (presence of air channels, transverse striations, etc.). Infrared microspectroscopy (IMS) is also usually conducted on the fiber and compared to a spectral database for an identification of fiber type. Solubility determinations in various solvents, as well as melting point temperatures, may also be helpful in fiber identification and comparison. Each of these procedures was assessed for all fibers every eight weeks for two years. In the sections below, a brief overview is given of each fiber property that was evaluated in this study.

Polarized Light Microscopy

Refractive index measurements for fibers were determined for the n-parallel ($n_{||}$) and n-perpendicular ($n_{\perp}$) of each fiber by means of the Becke-line immersion method. First, a Polytetrafluoroethylene (PTFE)-coated razor was used to cut a short (2 – 4mm) section of yarn from the fabric swatch. The fibers were gently teased apart with forceps and dissecting needles, then immersed in a certified refractive index liquid (Cargille Labs, Cedar Grove, NJ) on a clean microscope slide and covered with a coverslip. The fibers were then viewed with the PLM (polarizer aligned in the east – west orientation), and mounted in successive refractive index liquids until the edges of the fibers in the parallel or perpendicular orientation (relative to the polarizer) showed such low contrast that they appeared to “disappear” when illuminated with monochromatic sodium D light (589.3 nm). The temperature was noted via a calibrated digital thermometer (Control Company, Friendswood, TX) atop the microscope stage, and the refractive index was temperature-corrected according to the equation printed on the

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corresponding refractive index liquid bottle. Birefringence was calculated as the numerical difference between $n_{||}$ and $n_{\perp}$. The sign of elongation was also determined based on refractive index results: the sign of elongation is positive (+) if $n_{||} > n_{\perp}$, and negative (-) if $n_{||} < n_{\perp}$. Any changes in these optical properties may indicate fiber degradation, and were included as PLM observations every eight weeks.

Pleochroism (or dichroism) in fibers refers to an apparent change in color as a fiber is rotated when viewed with the PLM in plane-polarized light. This color change is a result of preferential absorbance of different wavelengths along different vibration directions. Many fibers, including manufactured fibers of natural origin are dyed or pigmented with colorants that can become oriented within the fiber. Changes in absorbance color can be seen with the PLM on fibers colored with certain dyes and pigments. Although some of the fibers used in this study were colored, none were pleochroic. However, this optical property was monitored for any changes throughout the study.

Manufactured fibers, including those examined here, always display parallel extinction, i.e., their principal vibration directions are always aligned parallel to the major axes of the fiber. Thus when viewed between crossed polars, the fibers appear darkest when they are aligned with the privileged directions of the analyzer and polarizer: north – south or east – west. Extinction in manufactured fibers can be described as complete or partial in quality. Any changes in extinction for the duration of this project were noted.

Fourier-Transform Infrared Microspectroscopy (IMS)

Infrared spectra were collected every eight weeks using an IlluminatIR (Smiths Detection, Edgewood, MD), a dedicated FTIR microspectrometer attached to a microscope. The instrument is equipped with an Attenuated Total Reflectance (ATR) objective, which allows the examiner to obtain an infrared spectrum of a single fiber when the objective is pressed into the

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fiber. Minimal sample preparation was required: 2 – 4mm sections of yarn from the fabric swatches were cut with a PTFE-coated razor blade, then teased apart as individual fibers on a microscope slide. The target fiber was first brought into focus, then the ATR objective was lowered and pressed into the fiber and the infrared spectrum was collected using QualID software (Smiths Detection, Edgewood, MD). As with the PLM observations, data were collected in duplicate by two separate analysts. Spectra were compared at various time points via SynchronizIR software (Smiths Detection, Edgewood, MD) for any observable differences.

Solubility

Solubility was determined using seven solvents commonly used in forensic laboratories: formic acid, chloroform, glacial acetic acid, acetone, dimethylformamide (DMF), concentrated sulfuric acid, and concentrated nitric acid. Short, 2 – 4mm sections of yarn were cut from the swatch with a PTFE-coated razor blade, and teased apart onto a clean glass microscope slide. After coverslipping, the fibers were observed through the microscope while a drop of the chosen solvent was added to the edge of the coverslip and allowed to run underneath and contact the fibers. The fibers were observed for one minute and, depending upon any physical changes that were observed, described as “soluble,” “insoluble,” “partially soluble,” or “swells.” Additionally, any emission of gas bubbles, a color change, or gelling was noted.

Melting Point

Melting point was determined microscopically using a calibrated microscope hotstage, the Mettler FP-5 (Mettler-Toledo, Columbus, OH), capable of a temperature range between 25°C and 300°C. Short (2 – 4mm) sections of yarn were cut with a PTFE-coated razor blade, and individual fibers were teased apart and placed on one end of a glass slide. Dow Corning 710 silicone oil was used as a mounting medium in order to ensure an accurate, reproducible melting point (10,11). The slide was inserted into the hotstage at approximately 10°C below the

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expected start of melting. The preparation was heated at 3°C per minute and observed between crossed polars with the first order red compensator inserted for contrast. The temperature at which the fibers began to react, either via shrinkage or decreased retardation was recorded, along with the melting point, where the fibers reached isotropy. Three runs were performed by one analyst, and then the procedure was repeated once by a second analyst. If the melt start and end values were not within 5°C of the first analyst's numbers, two additional runs were performed. The melting point and various other temperature effects (such as shrinkage) are often useful when comparing known and questioned fibers, and any significant changes were hypothesized to be indicative of fiber degradation.

Results and Discussion

Viscose Rayon

All viscose fabrics had similar properties at week 0 (Table 2): $n_{||} = 1.55$, $n_{\perp} = 1.52$, with a birefringence of 0.029 – 0.035, exhibited parallel extinction with some partial (undulose) extinction, and a positive sign of elongation. Fibers were 10 – 25µm wide, and all demonstrated the longitudinal striations typical of viscose rayon with a multi-lobed cross-section (Figure 1). A typical infrared spectrum is shown in Figure 2. Melting point and solubility data are shown in Table 3. Viscose does not melt below 300°C; rather, the fibers char and discolor to brown as they are heated. The fibers are insoluble in formic acid, chloroform, acetic acid, acetone, and DMF. Viscose fibers are soluble in concentrated sulfuric acid, and swell to about twice the size in concentrated nitric acid.

Viscose fabrics present in the composter, freshwater, and saltwater environments began to decompose relatively quickly. In fact, at the first eight-week benchmark for PLM and IR analyses, V2 and V3 swatches in the composter, freshwater, and saltwater environs, as well as V5 saltwater and V1 composter had no recognizable viscose fibers remaining. Viscose fibers

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for other swatches in these three environments were present, but macerated and dilapidated. The fibers looked almost like natural fibers: they had lost the longitudinal striations that are typical of multi-lobed rayon, and transverse markings were visible on some (Figures 3 and 4). However, refractive indices and IR spectra were consistent with cellulose at this point. The viscose fibers in the water environments eventually form an isotropic, glassy lump (Figure 5) that is no longer cellulosic, and refractive indices and IR spectra cannot be used for identification. In order to more precisely track the degradation of the viscose, the experiment was repeated for all five viscose swatches in the composter, freshwater, and saltwater, with analyses every two weeks (week 2, week 4, week 6, and week 8 repeated). Table 4 summarizes the degradation times for these swatches. Although the sample size here is rather small, a general pattern emerges, whereby the swatches with a lower percentage of viscose see the complete loss of recognizable viscose fibers earlier than swatches with higher percentages. After four weeks of exposure, the V2 swatch (15% viscose), which contained the lowest proportion of viscose, had no recognizable viscose fibers present in the composter or freshwater, with very few, extremely beat-up fibers found in the saltwater. V3 (34% viscose) had no recognizable fibers in the composter or saltwater at six weeks, and those in the freshwater were very macerated and on their way out as well. There were two week 8 assessments (the original and the repeat), and while similar, the data didn't always agree perfectly. At the first week 8 assessment, V5 (70% viscose) had recognizable, though tattered, viscose fibers in the freshwater and the composter, but none in the saltwater. At the week 8 repeat, however, viscose fibers were found in the saltwater environment, though they were extremely beat up. A similar occurrence was observed with V1 (100% viscose): the first week 8 assessment revealed no recognizable fibers in the composter, along with macerated fibers in the water environments; the week 8 repeat found no recognizable fibers in the saltwater, but there were some macerated fibers in the composter and freshwater. V4 (92% viscose) persisted the longest, with fibers lasting in each environment through both week 8 assessments.

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By week 16, however, no recognizable fibers were found in the composter or saltwater; fibers endured in the freshwater up through week 40, and were gone by week 48. Viscose fabrics in the oven, freezer, and UV environments persisted for the entire length of the study.

Two viscose swatches, V2 and V5, exposed to UV light developed small, dark speckled areas on some fibers (Figure 6). These “freckles” were sub-micron, with variations in size. The freckles were not uniformly distributed along the length of the fiber, and some sections were densely freckled while others were completely clear. This irregularity is likely due to the fact that the fibers were woven into a fabric, and thus overlapping yarns offered protection from the UV light. Initial concern that these freckles affected refractive index was assuaged by performing dispersion staining on the fibers. Both freckled and non-freckled areas of the fibers gave the same dispersion staining colors, and thus have the same refractive index. It is unclear why three of the five viscose swatches did not form the freckles. None of the viscose swatches were delustered, and although V2 is colored light pink, V5 appears to be undyed. V2 is a blend of 59% silk, 26% nylon, and 15% viscose, while V5 is a blend of 70% viscose (from bamboo), 25% cotton, and 5% spandex. The freckles were first seen on both V2 and V5 at week 8, and gradually increased in concentration over time. In order to more closely examine the freckles, the fibers were polished with an ion mill, and then imaged with a scanning electron microscope (SEM) (Figures 7 and 8). The images indicate that the freckles are internal air or gas pockets, and are not present on the fiber surface. Their mechanism of formation is unclear, and may warrant further study. It is also possible that the development of the freckles is related to the cellulose source material (softwood, cotton linters, bamboo, etc.), and that different cellulose sources are more prone to freckling.

To test how well the UV lamp compared to sunlight, the V2 and V5 swatches were sent to a colleague in southern California for exposure to the sun. The swatches were stapled to a 2x4 piece of wood and mounted on a fence. Initially, the swatches faced south, but then were moved to a sunnier location with an eastern exposure four weeks later. Daily UV Index ratings

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for the ZIP code were logged. In the period between 12 May – 01 September 2014 (16 weeks) ranged from 8 – 12. As was seen in the swatches under the UV lamp, the freckles appeared in both V2 and V5 swatches by week 8, which indicates that the UV lamp in the laboratory is a reasonable approximation of sunlight.

The swatches remaining in the other environments showed no appreciable differences in optical properties, infrared spectra, solubility, or melting point for the duration of the study.

Azlon

All azlon fabrics had similar properties at week 0 (Table 2): $n_{||} = 1.55$, $n_{\perp} = 1.52$, with a birefringence of 0.021 – 0.026. These values are consistent with the modern generation of azlons (12), compared to the azlons produced prior to the 1950s, which had much lower birefringence values of 0 – 0.006 (13). The fibers exhibited parallel extinction with some partial (undulose) extinction. The signs of elongation were positive. Fibers were 10 – 25μm wide. A1 – A4 contained internal rectangular voids (Figure 9); A5 also contained voids, but they were smaller and streakier in appearance (Figure 10). A typical infrared spectrum is shown in Figure 11. Melting point and solubility data are shown in Table 3. Azlon's melting point behavior was somewhat complex. The onset of melting was straightforward, and the fibers began to crimp and shrink, around 230°C. However, if the fiber of interest was stuck to another fiber, or otherwise pinned down onto the slide and unable to move freely, the fiber never reached isotropy below 300°C. Furthermore, even at isotropy, the fibers never lost their shape. Thus, when determining the final melting point, it was important to look at short, individual fibers that were not obstructed by other fibers or trapped in the preparation. Average melting points ranged from about 260 – 280°C. Azlon swelled to about four times its size in formic acid, and was insoluble in chloroform, acetic acid, acetone, and DMF. It was partially soluble in

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concentrated sulfuric and nitric acids: the fibers splintered and broke apart, but did not completely dissolve, and gas bubbles were released.

Azlon fibers were relatively stable across all six environments, and no significant changes were noted in optical properties, infrared spectra, melting behavior, or solubility. However, morphological changes were seen in two swatches: the rectangular, elongated inclusions within A1 and A3 in both water environments appeared to collapse and become streakier in appearance (Figure 12). These changes were visible on some fibers as early as week 16 for A3, but weren't seen until week 32 in A1. This was not observed in the other azlons, and the cause is unknown. Some azlon manufacturers are known to apply antibacterial finishes to their fibers, in addition to other softening or anti-wrinkle treatments (3). These procedures may play a role in the differences seen here.

Polylactic Acid (PLA)

All PLA swatches had similar optical properties at week 0 (Table 2), with $n_{||} = 1.47$, $n_{\perp} = 1.44$, and birefringence between 0.026 – 0.030. Extinction was parallel, with some partial (undulose) extinction, and positive elongation. Fiber widths ranged from 10 – 30µm. Titanium dioxide (the anatase polymorph was identified by Raman spectroscopy) delusterant was present in P1, P3, P4, and P5. Differences between the fabrics were seen in fiber morphology. Some fibers were very smooth and relatively featureless, though crosshatching and fisheyes were often present in these fibers. Other fibers displayed transverse striations. These striations are dark and by transmitted light the fibers appear dark brown or tan (Figure 13). This pseudo-opacity is likely due to the poor alignment of the polymer chains in that area of the fiber, and may be an artifact of the extrusion process (7).

No significant changes in optical properties or IR spectra were observed throughout the study (Figure 14). However, morphological changes were observed in P1 and P3 swatches

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exposed to UV light. Beginning around week 8, these two swatches began to show voids within the interior of the fiber (Figure 15). The voids are likely a result of photodegradation, which occurs when the polymer absorbs light energy and initiates chemical reactions such as cross-linking, oxidation, or bond cleavage (14). Most of these inclusions were 1μm in size (though a few were as large as 2μm), and became more numerous over time. The exact cause of the voids is unknown, though it is unlikely that they are entirely related to the presence of titanium dioxide (TiO_2): Two other swatches, P4 and P5, contain the same TiO_2 polymorph, anatase, as verified by Raman spectroscopy, and the air pockets do not develop within these fibers. Photostabilizers are commonly added to polymers in order to combat photodegradation (14) and it is possible that the unaffected fibers have been treated to avoid such problems. Ion milling and subsequent SEM imaging were performed on the P1 and P3 fibers, which confirmed that these voids were air-filled cavities (Figures 16 and 17). In addition, swatches of P1 and P3 were sent to southern California and placed in the sun with the V2 and V5 swatches mentioned above. These fibers also show similar voids beginning at 8 weeks, again indicating that the UV lamp in the laboratory is a reasonable approximation of real sunlight.

Nearly all the fibers for the duration of the study behaved the same during melting point determinations (Table 3). At the onset of the melt, around 160°C, the fiber suddenly and abruptly shrunk, then gradually the retardation colors decreased to isotropy, for a melting point of around 170°C. However, at weeks 79 and 105, the PLA swatches in the oven environment no longer experienced the sudden shrinkage at the melt start. Instead, the retardation colors gradually decreased with little to no shrinkage occurring. The melting point values were not affected.

Solubility was unchanged across all environments for the length of the study. All swatches, regardless of environment, were soluble in chloroform, concentrated sulfuric acid, and concentrated nitric acid, in which the fibers softened to a gel. Swatches P1 – P5 were

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insoluble in formic acid, acetic acid, and acetone. Swatches P6 and P7 were also insoluble in formic acid and acetic acid, but were slightly soluble in acetone; the fibers swelled, frayed, and appeared textured.

Summary and Conclusions

The three fiber types chosen, viscose rayon, azlon, and PLA, are all comprised of biological polymers, and thus were expected to show significant changes after exposure to various environmental conditions. Instead, the fibers (especially the azlons and PLAs) displayed a remarkable amount of resiliency.

Viscose rayon degraded the fastest and most completely in the composter and the two water environments, with one swatch showing total loss of viscose as early as week 4. Remaining swatches had no recognizable viscose fibers by week 24, except for one swatch in the freshwater, in which viscose persisted until week 48. Several factors likely play a role in the speed of the degradation, including the percentage and amount of viscose fibers present, as well as the character of the weave. The fabric that persisted the longest had a tighter, denser knit than the other fabrics. As the viscose fibers degraded, they lost the longitudinal striations that are typical of rayon, and developed transverse markings and irregular edges. In fact, the fibers looked more like a natural fiber such as linen or jute, and could easily be mistaken as such. Refractive indices and IR spectra remain consistent as long as the fiber is recognizable. Eventually, the fibers lose all identifiable features as they form a glassy, non-fibrous globule. At this point, refractive indices are IR spectra cannot be used to identify the fiber.

All of the PLA swatches and three of the five azlon swatches were unchanged by the freshwater, saltwater, and composter exposures. Two of the azlon swatches did show a morphological change in the water environments: one by week 16 and the other by week 32. The rectangular inclusions within the fibers appeared to have collapsed, and the fibers took on a

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wrinkled or streaky appearance. Optical properties, melting point, and solubility were unchanged.

Under ultraviolet light, two of the five viscose swatches began to show a proliferation of small, dark freckles after 8 weeks of exposure. The freckles were not evenly distributed along the entire length of the fiber, nor were they present on all fibers, which is likely a result of shielding from overlapping fibers within the woven fabric. Two of the seven PLA fabrics developed voids starting at week 8; these voids became more numerous over time. Optical properties, solubilities, and melting points were unaffected.

No changes were seen in any of the fibers in the cold environment, and only a minor change was noted in the oven environment: during melting point determinations, the PLAs typically shrink noticeably at the onset of melting; however, by week 79, the PLAs in the oven no longer shrunk, and instead a gradual decrease in retardation colors signaled the start of melting.

There are certain practical aspects for the forensic fiber examiner culminating from this research. With regards to fiber identification, the optical properties, IR spectra, solubilities, and melting points of viscose, azlon, and PLA are largely unchanged across the various environments. As long as a fiber is present and its properties can be measured, the fiber type is determinable. Even as the viscose fibers degraded in the water and composter environments, their refractive indices and IR spectra remained consistent. It is only once the fibers formed a glassy, isotropic coagulation that traditional forensic science methods may not be useful in identifying the former viscose.

Regarding forensic fiber comparisons, the effects of ultraviolet light have been shown on several viscose rayon and PLA fibers, and water submersion has been shown to affect one of the azlons. These findings may explain any differences that might be observed in Questioned and Known fibers submitted as forensic evidence, if the Q and K samples were known to be in different environments over a period of time. In addition, these results may potentially

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strengthen an association if the same morphological changes are seen on both the Questioned and Known fibers.

Small samples of the fabrics used in this study are available to forensic science laboratories on request. Please contact Kelly Brinsko for additional details.

Acknowledgements

The authors would like to thank Dr. Gary J. Laughlin for his guidance and assistance throughout the project; Skip Palenik and Jason Beckert of Microtrace for the Raman Microspectroscopy of PLA fibers; Rich Brown of MVA for ion milling and SEM imaging; Wayne Moorehead and Aletha Basconcillo for exposing fabrics to southern California sunshine; Colin Booth for maintenance of water tanks.

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Figures

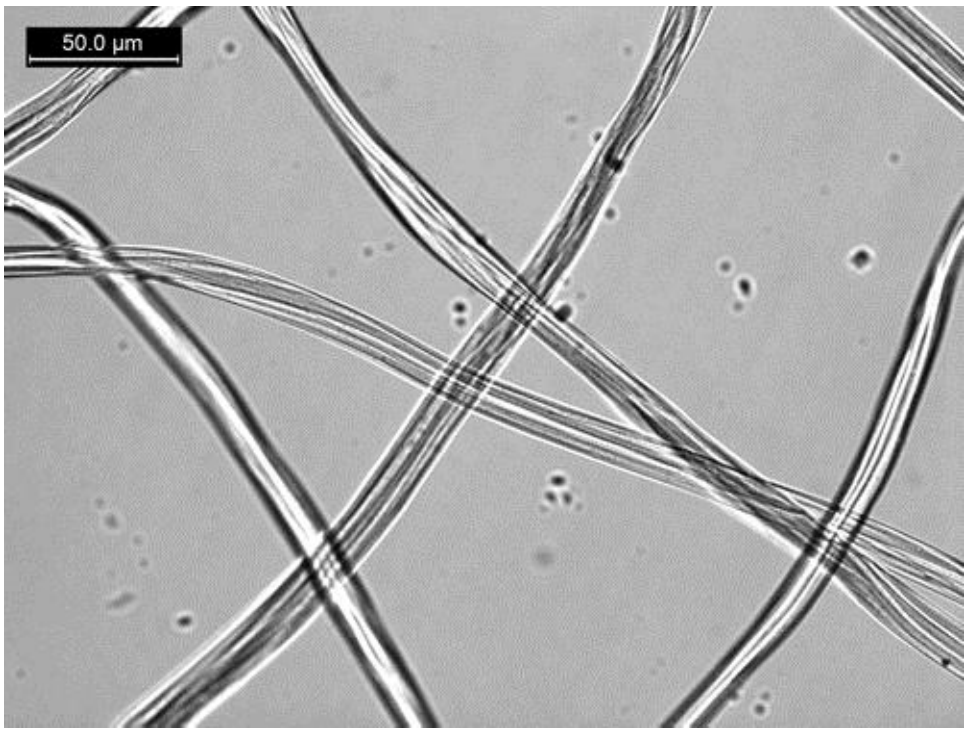

Figure 1. Plane polarized light image of viscose rayon control sample.

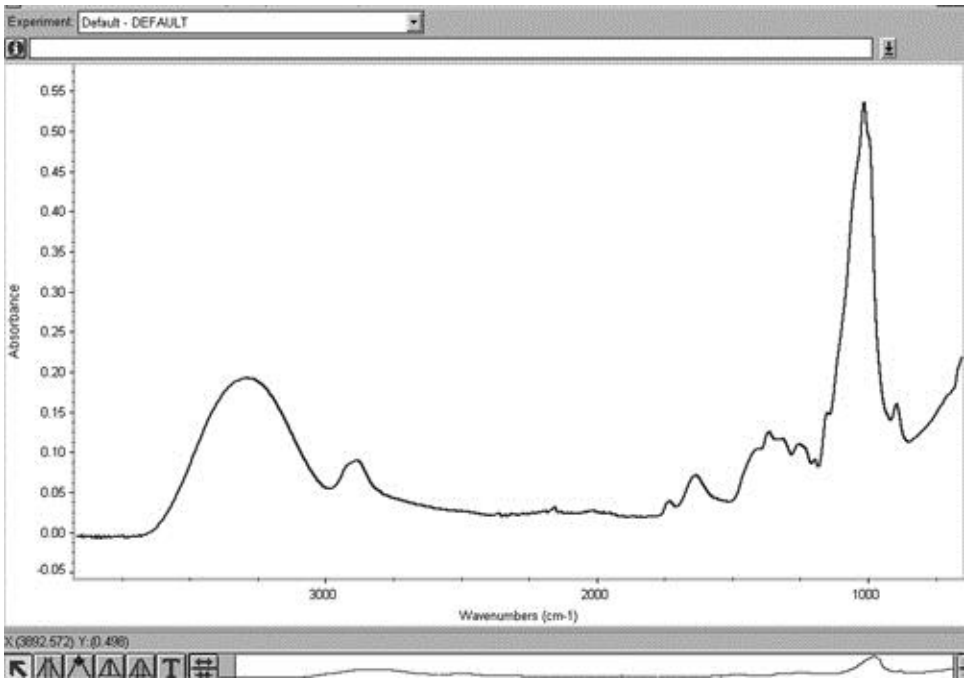

Figure 2. Infrared spectrum of viscose rayon showing typical absorption peaks.

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Figure 3. Plane polarized light image of a macerated viscose rayon fiber.

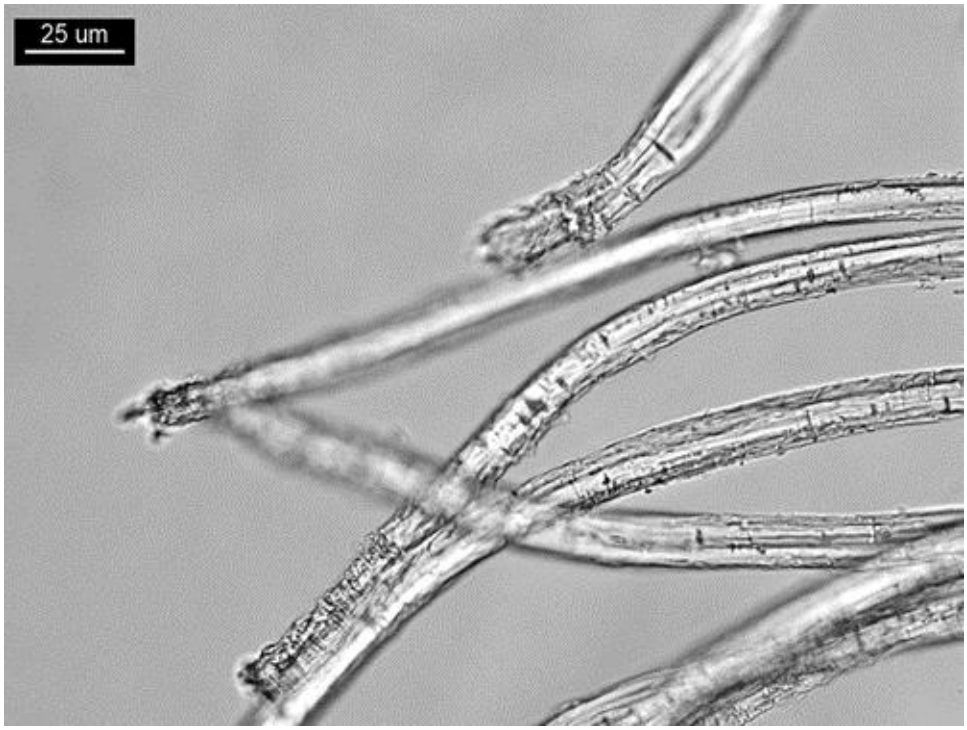

Figure 4. Plane polarized light image of viscose rayon fibers showing fading of longitudinal striations along and the introduction of transverse markings typical of natural fibers.

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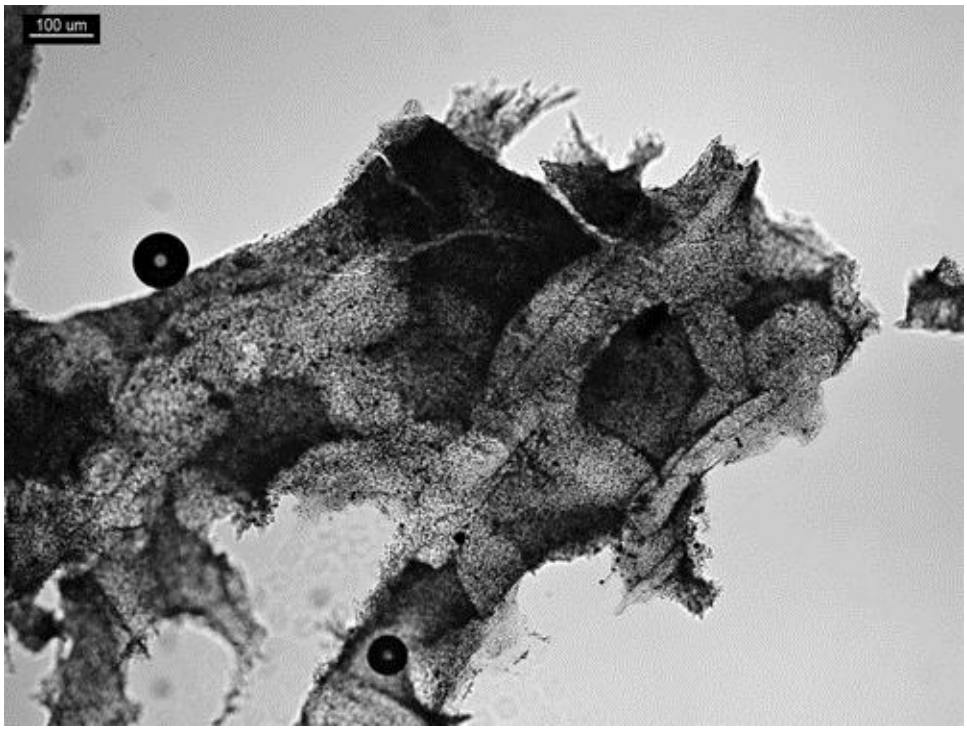

Figure 5. Plane polarized light image of viscose fibers from the freshwater environment after 48-week period.

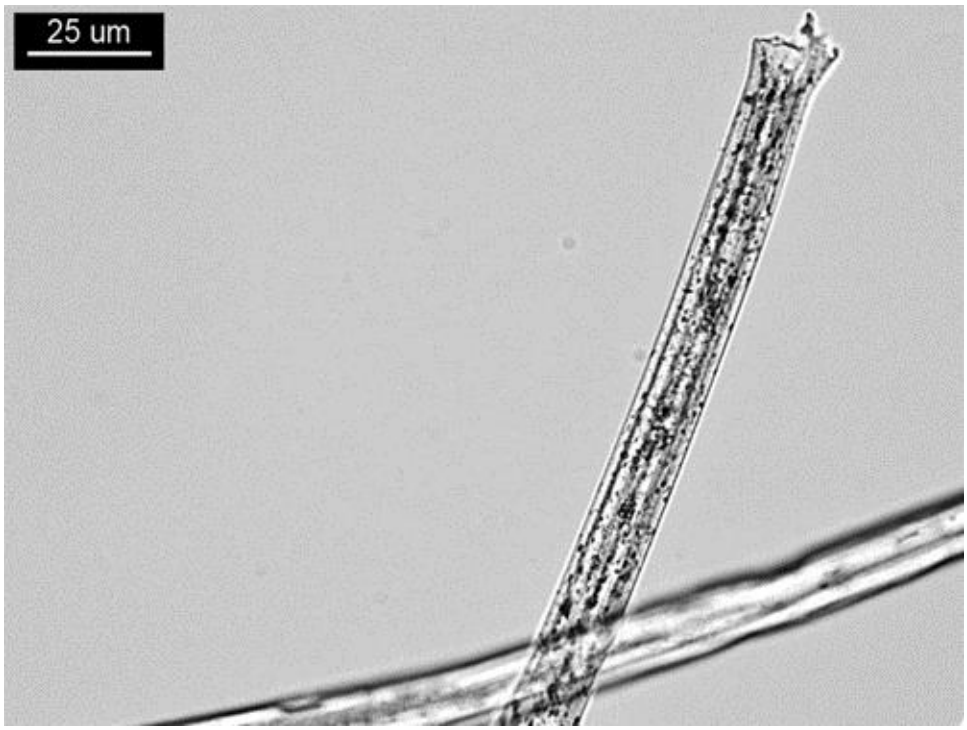

Figure 6. Viscose rayon fiber showing dark speckled areas due to UV exposure (104 weeks).

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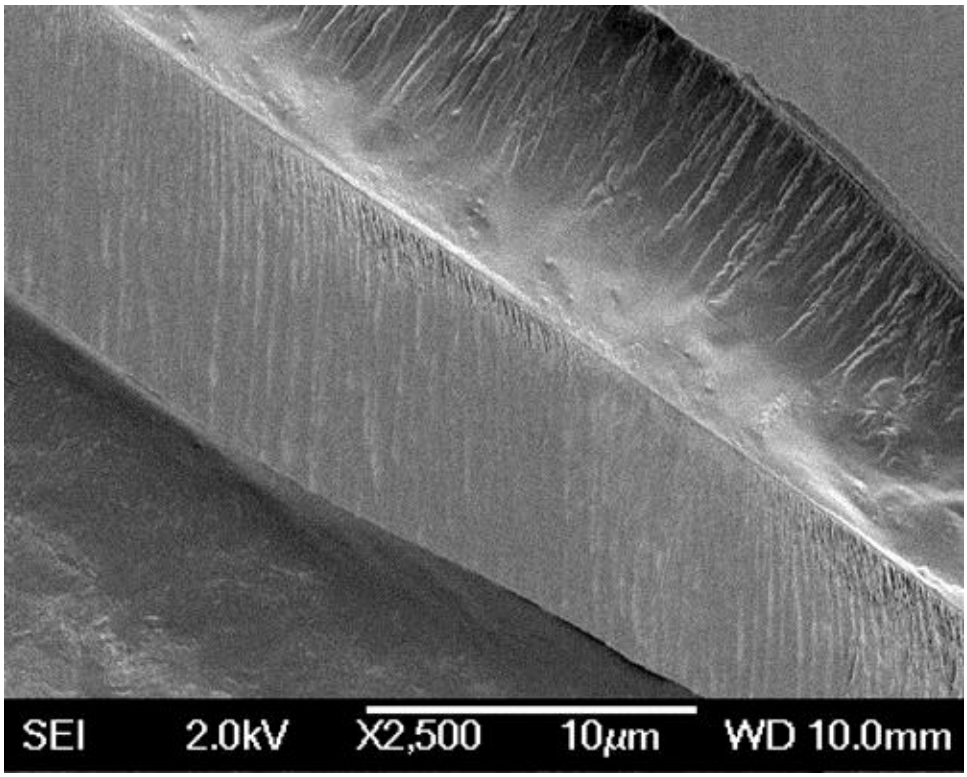

Figure 7. SEM image of ion milled viscose rayon control sample.

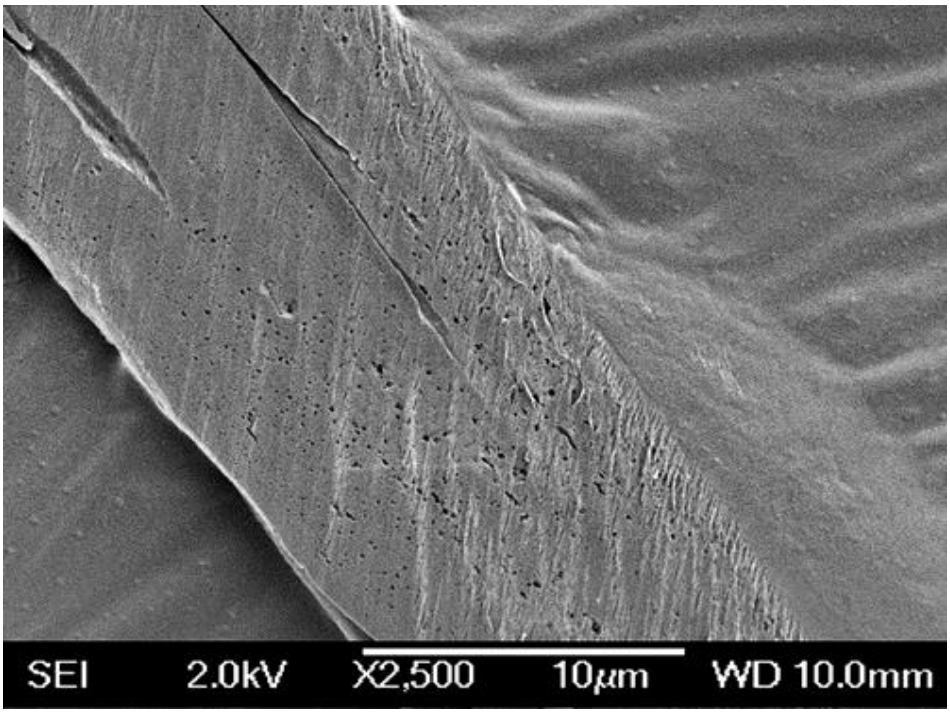

Figure 8. SEM image of ion milled viscose rayon after 88 weeks of UV exposure showing “freckles” as pockets.

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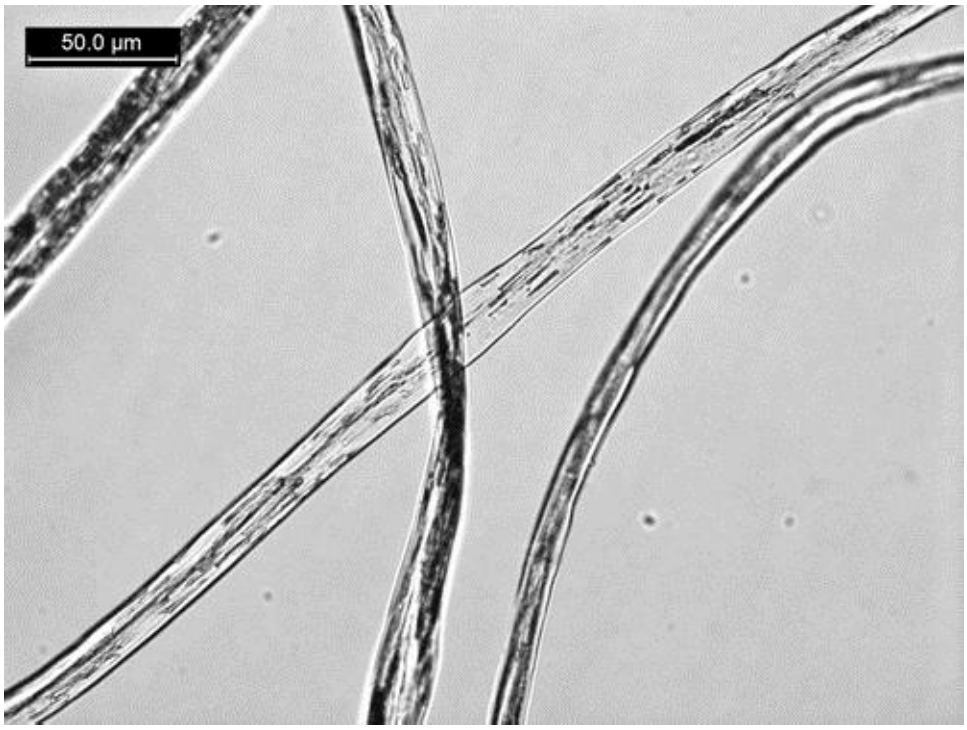

Figure 9. Plane polarized light image of A3 control sample.

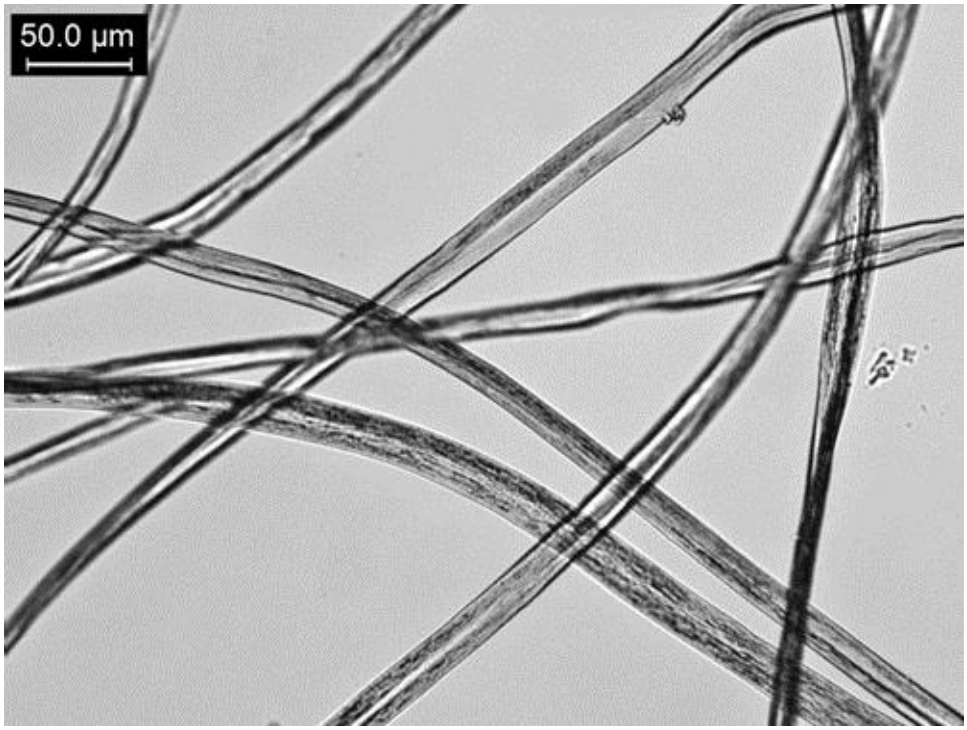

Figure 10. Plane polarized light image of A5 control sample.

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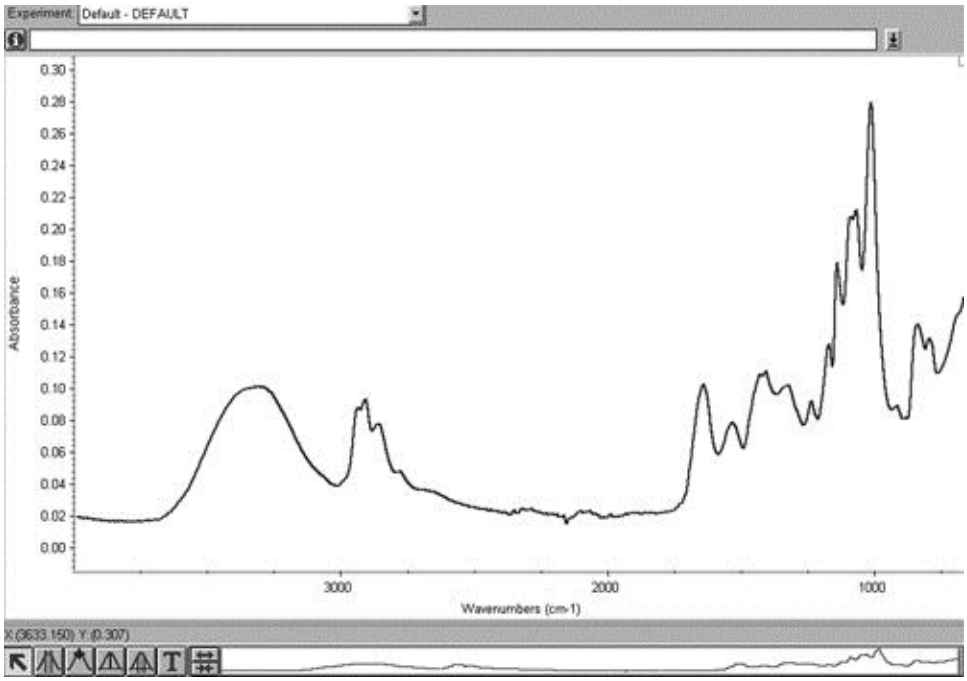

Figure 11. Infrared spectrum of azlon showing typical absorption peaks.

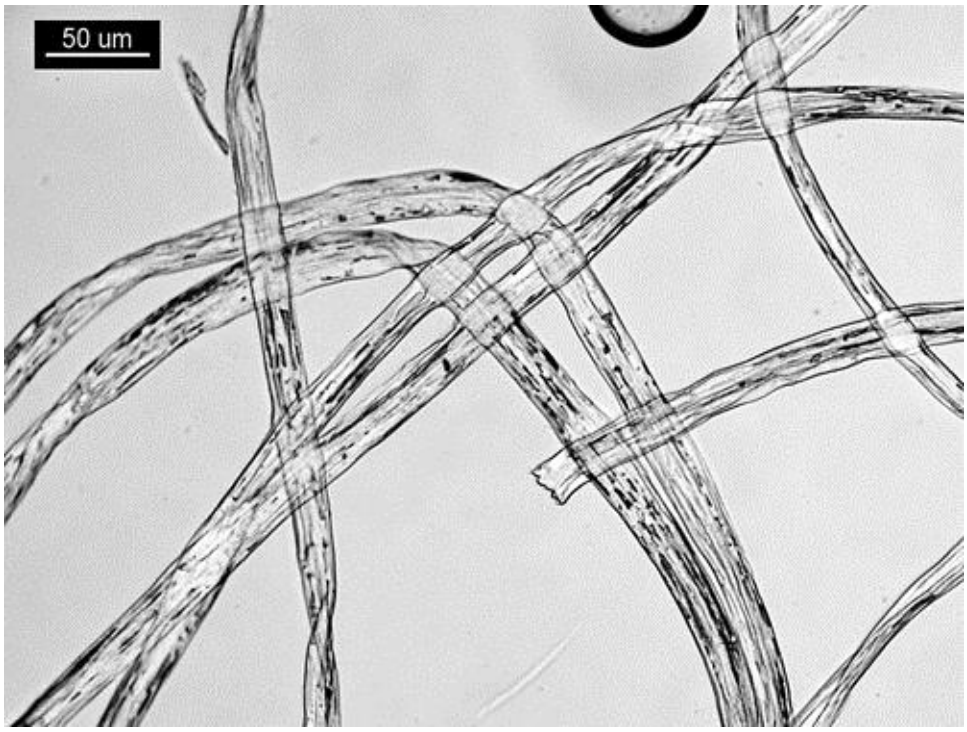

Figure 12. Plane polarized light image of A3 fibers after 24 weeks of freshwater submersion showing rectangular, elongated inclusions.

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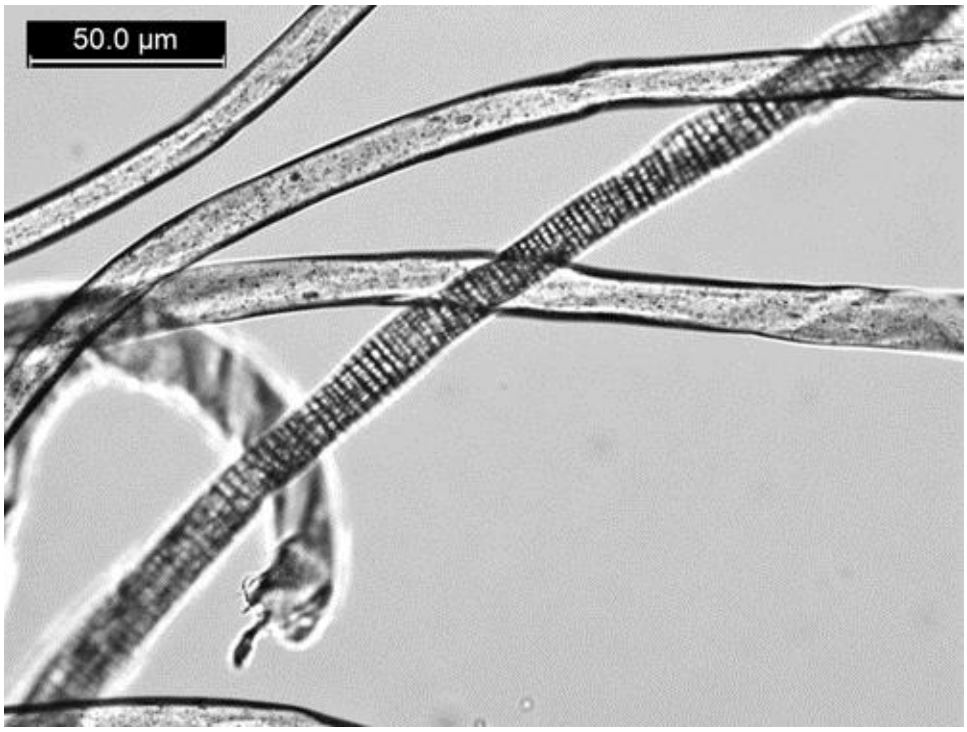

Figure 13. Plane polarized light image of PLA fiber showing dark, transverse striations.

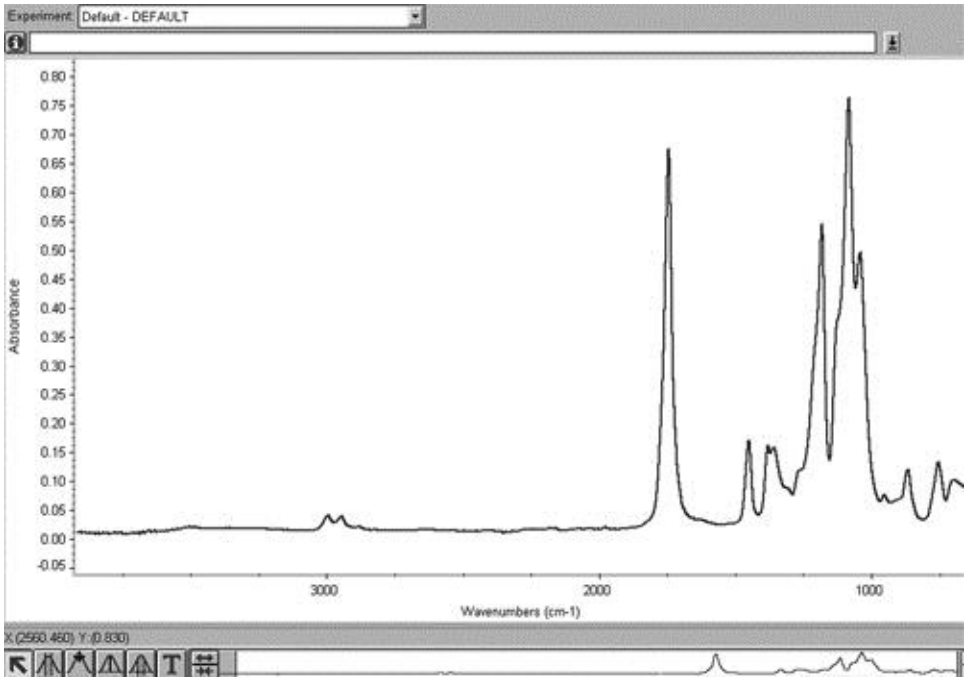

Figure 14. Infrared spectrum of PLA showing typical absorption peaks.

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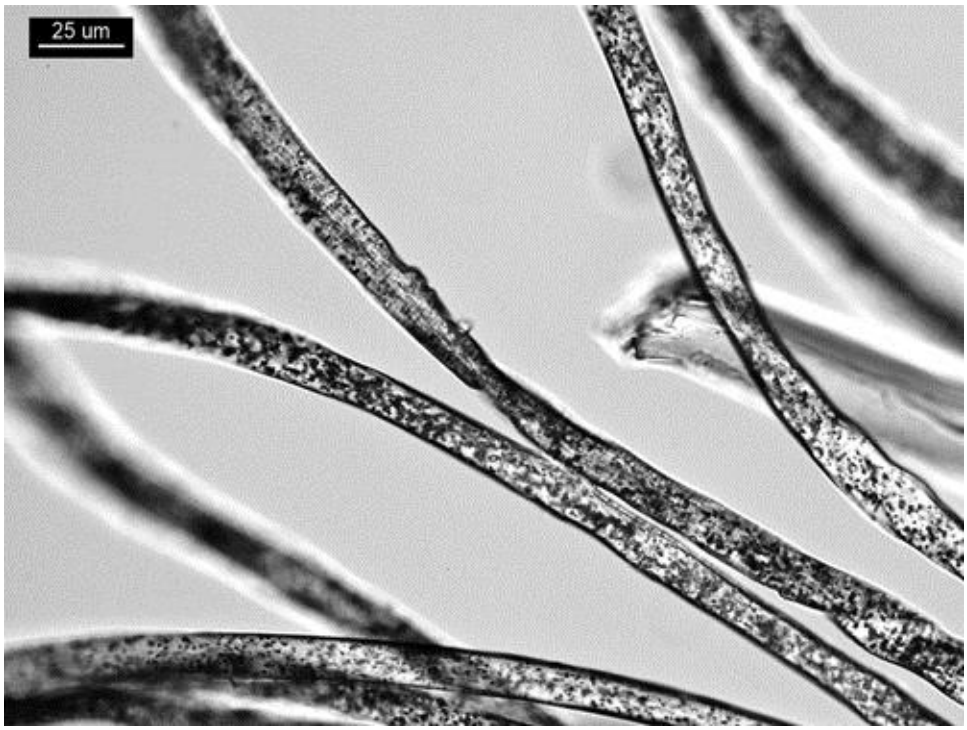

Figure 15. Plane polarized light image of PLA showing voids within the interior of the fiber.

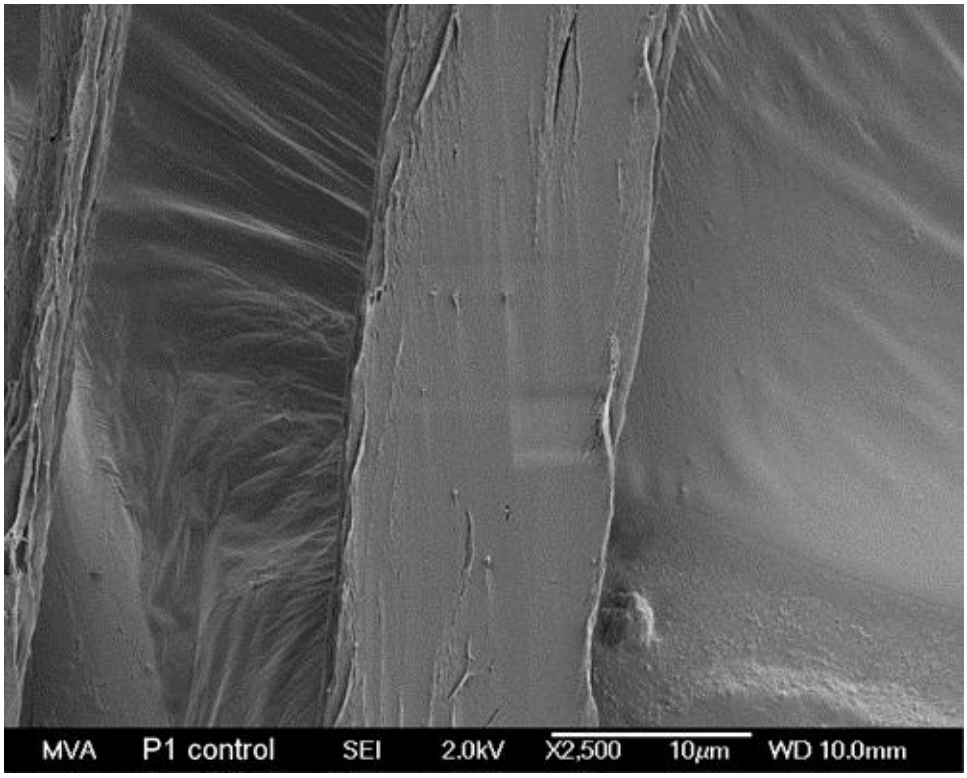

Figure 16. SEM image of ion milled PLA control sample.

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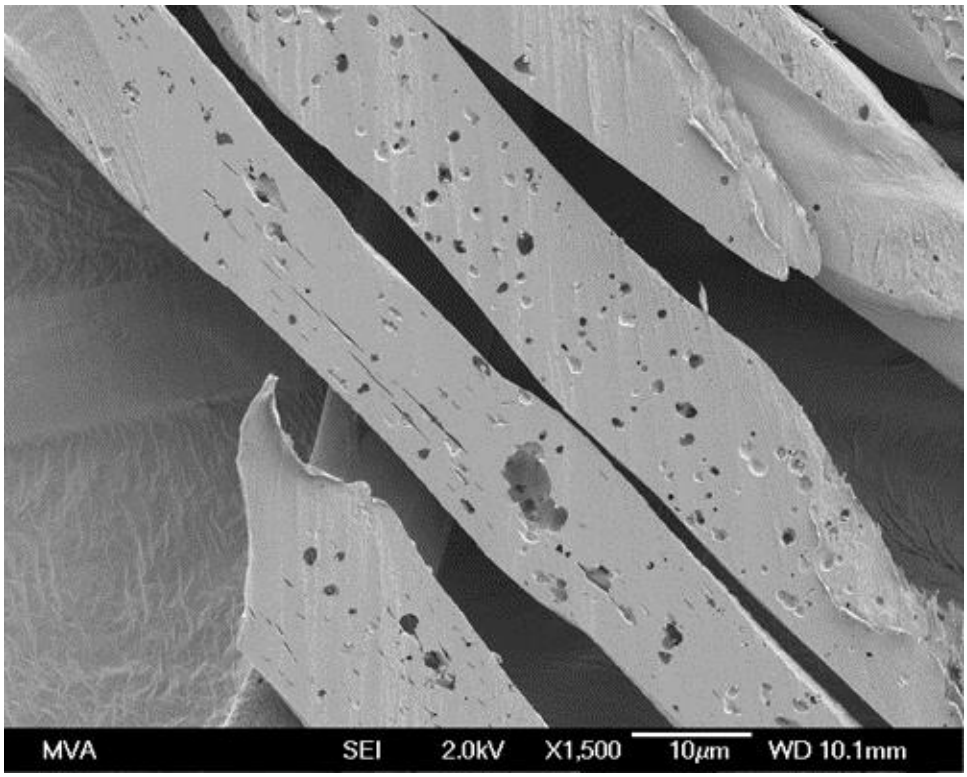

Figure 17. SEM image of ion milled PLA after XX weeks of UV exposure showing “freckles” as pockets.

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Tables

Table 1

Fiber Type	MFNO No.	Item	Color	Purchased From	Brand Name	Country of Manufacture (as labeled)	Fabric content (as labeled)
Azlon	A1	Sweater	Mauve	Sierra Trading Post	Exoffico	China	85% Azlon, 15% Cashmere
Azlon	A2	Polo shirt	Light green	faeriesdance.com	Of The Earth	China	40% Azlon, 55% Cotton, 5% Spandex
Azlon	A3	Camisole	Cream	faeriesdance.com	Dream Designs	China	94% Soy, 6% Spandex
Azlon	A4	Jacket	Blue	eBay.com	Kavu	China	53% Azlon, 44% Cotton, 3% Spandex
Azlon	A5	Scarf	Pink, Purple	eBay.com	Talbots	India	98% Azlon, 2% "Metallic"
Viscose	V1	Shirt	Mauve	Nordstrom.com	Trouve	China	100% Viscose
Viscose	V2	Sweater	pink	Amazon.com	Jones New York	China	59% silk, 26% nylon, 15% viscose
Viscose	V3	Cardigan	Ivory	Nordstrom.com	Bobeau	USA	34% Rayon, 63% Polyester, 3% Spandex
Viscose	V4	Shirt	Ivory	Zappos.com	Three dots	USA (imported fabric)	92% viscose, 8% spandex
Viscose (Bamboo)	V5	Tank top	white	Amazon.com	Green Apple	Mexico	70% Bamboo viscose, 25% organic cotton, 5% spandex
PLA	P1	Shirt	White	eBay.com	From RN#: "Future Products Inc"	USA	100% Ingeo
PLA	P2	Waffle Weave fabric	White	CoplandFabrics.com	Copland Fabrics	USA	100% Ingeo
PLA	P3	Batiste fabric	White	CoplandFabrics.com	Copland Fabrics	USA	100% Ingeo
PLA	P4	Twill shirt	Bone	Green Logo World	Ingeo	China	100% Ingeo
PLA	P5	Polo shirt	White	Green Logo World	Ingeo	India	100% Ingeo
PLA	P6	Socks	White, pink, gray	Zappos.com	Fox River	USA	40% nylon, 37% ingeo, 21% recycled polyester, 2% spandex
PLA	P7	Socks	white, grey	REI.com	REI	USA	70% Ingeo PLA fiber, 28% nylon, 2% spandex

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Table 2

Fabric	$n_{\parallel}$	$n_{\perp}$	Birefringence	Color	Extinction	Sign of Elong.	Size Range (µm)	PLM Notes	Special Issues
A1	1.545 - 1.554	1.518 - 1.527	0.021 - 0.03	pink, non pleochroic	parallel, complete & undulose	(+)	5 - 25	Abundant rectangular inclusions/air bubbles. Not all fibers have uniform RI but all very close	Water environments start to become streaky, inclusions/air bubbles begin to collapse around week 32. Surfaces of oven fibers begin to crack/fracture around week 88.
A2	1.544 - 1.553	1.521 - 1.527	0.021 - 0.029	colorless to pale green, non pleochroic	parallel, complete & undulose	(+)	7.5 - 25	Fibers flat, elongated inclusions. Not all fibers have uniform RI but all very close.	Rectangular inclusions persist at least up to 104 weeks
A3	1.543 - 1.552	1.517 - 1.527	0.020 - 0.030	colorless	parallel, complete & undulose	(+)	5 - 30	Fibers flat, likely bean shaped crossection, elongated inclusions. Not all fibers have uniform RI but all very close	Inclusions start to become streaky in salt and freshwater @ wk 16.
A4	1.545 - 1.553	1.520 - 1.527	0.020 - .029	blue/light blue, non pleochroic	parallel, complete & undulose	(+)	7.5 - 30	Abundant rectangular inclusions/air bubbles though not evenly distributed throughout. Not all fibers have uniform RI but all very close	Rectangular inclusions persist at least up to 104 weeks
A5	1.542 - 1.557	1.521 - 1.529	0.018 - 0.030	pink	parallel, complete & undulose	(+)	5 - 30	Less air bubbles/inclusions than A1-A4, fibers look "textured". Not all fibers have uniform RI but all very close.	Never had rectangular inclusions; does not become streaky.
P1	1.470 - 1.475	1.442 - 1.446	0.028 - 0.030	colorless	parallel, complete & undulose	(+)	7.5 - 25	Some variance in fiber morphology - some "smooth" with small particles of delusterant (anatase) in them while others have fisheyes or transverse striations, resulting in some pseudo-opaqueness (a tan color).	Fibers in UV developed small air voids in interior of fiber, increasing in size over time, initial onset @ 16 weeks. Broken fibers wk 104 oven
P2	1.471 - 1.476	1.442 - 1.446	0.027 - 0.032	colorless	parallel, complete & undulose	(+)	15 - 30	Fibers smooth, some crosshatching, some fisheyes and small black inclusuons. Crossection circular, slightly angular or spiral twist.	Cracks noted in wk 16 oven and UV also in wk 64 oven noted as beat up and broken, break easily wk 104 and week 96 composter
P3	1.472 - 1.477	1.442 - 1.446	0.026 - 0.034	colorless	parallel, complete & undulose (small dull fibers)	(+)	7.5 - 20, 20 - 35	Delusterant present (anatase). 2 morphologies: larger bright fibers with little to no delusterant, smaller dull fibers with abundant delusterant. Transverse striations resulting in some pseudo-opaqueness (a tan color) those without have complete parallel extinction. Croshatches visible.	Fibers in UV developed small air voids increasing in size over time, initial onset @ 16 weeks. Broken fibers wk 104 oven.
P4	1.471 - 1.476	1.442 - 1.447	0.027 - 0.032	colorless	parallel, complete & undulose	(+)	10 - 20	Some transvers striations and fisheyes. Delusterant present (anatase). Some fibers straight and smooth, others have spiral twist.	Some fisheyes appear to increase in size over time. Wk 104 oven fibers break easily.

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Table 2 Continued

Fabric	$n_{\parallel}$	$n_{\square}$	Birefringence	Color	Extinction	Sign of Elong.	Size Range (µm)	PLM Notes	Special Issues
P5	1.471 - 1.476	1.443 - 1.447	0.027 - 0.031	colorless	parallel, complete & undulose	(+)	7 - 20	Some fibers smooth others have transverse striations resulting in some pseudo-opaqueness (a tan color). Fisheyes. Delusterant present (anatase)	Wk 104 oven fibers break easily.
P6	1.468 - 1.474	1.441 - 1.446	0.024 - 0.032	colorless	parallel, complete & undulose	(+)	7 - 30	Mix of smooth fibers and those with transverse striations (sometimes only along one side of fiber) resulting in some pseudo-opaqueness (a tan color). , fisheyes and crosshatching, small black inclusions	No signs of breakage in oven like P1-P5.
P7	1.468 - 1.474	1.441 - 1.446	0.024 - 0.030	colorless	parallel, complete & undulose	(+)	10 - 25	Mix of smooth fibers and those with transverse striations (sometimes only along one side of fiber), fisheyes or small balck inclusions.	Small amount of fiber breakage in wk 104 oven.
V1	1.549 - 1.562	1.518 - 1.528	0.028 - 0.036	pink	parallel, complete & undulose	(+)	7.5 - 20	Parallel striations typical of viscose.	Freshwater sample degradation onset by wk 2 also n's become difficult to match, consumed by wk 16. Saltwater sample degrading by wk 2, original swatch persisted to wk 8, repeat consumed by wk 8. Composter sample degrading by wk 4, original swatch consumed by wk 8, repeat found minimal viscose present @ wk 8, consumed by wk 16.
V2	1.551 - 1.564	1.518 - 1.530	0.029 - 0.034	colorless	parallel, complete & undulose	(+)	10 - 20	Parallel striations typical of viscose. Small black incusions, potentially delustered.	Freshwater degrading by wk 2, consumed by wk 4. Saltwater degrading by wk 2, repeat found minimal fibers present @ wk 6, original and repeat consumed by wk 8. Composter sample majorly degraded by wk 2 consumed by wk 4. "Freckle" onset wk 8 UV, freckled areas have lower n. Slight range of n's within some preps.
V3	1.549 - 1.560	1.517 - 1.530	0.027 - 0.036	colorless	parallel, complete & undulose	(+)	7.5 - 20	Parallel striations typical of viscose, some appear to have a "string of pearls" row of air bubbles near the center, parallel to the length.	Freshwater degrading by wk 2, consumed by wk 8 in original and repeat. Saltwater degrading by wk 2, consumed by wk 6. Composter sample degrading by wk 2, consumed by wk 4.
V4	1.552 - 1.564	1.518 - 1.530	0.028 - 0.036	colorless	parallel, complete & undulose	(+)	7.5 - 20	Parallel striations typical of viscose.	Freshwater degrading by wk 2, consumed by wk 48. Saltwater degrading by wk 2, consumed by wk 16. Composter degrading by wk 4 consumed by wk 16.
V5	1.549 - 1.561	1.519 - 1.529	0.028 - 0.036	colorless	parallel, complete & undulose	(+)	7.5 - 20	Parallel striations typical of viscose.	Freshwater degrading by wk 2, consumed by wk 24. Saltwater degrading by wk 2, original consumed by wk 8, repeat persisted to wk 8. Composter sample degrading by wk 4, consumed by wk 16. UV "freckle" onset wk 8.

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Table 3

Fabric	Solubility							Melting point °C			
	Formic Acid	Chloroform	AcOH	Acetone	DMF	H_2SO_4	HNO_3	Start (Average)	Standard Deviation	Finish (Average)	Standard Deviation
A1	Swells	I	I	I	I	Partially soluble, splinters, air bubbles	Partially soluble, splinters, air bubbles	228.8	2.8	271.0	12.0
A2	Swells	I	I	I	I	Partially soluble, splinters, air bubbles	Partially soluble, splinters, air bubbles	232.3	1.2	280.4	16.3
A3	Swells	I	I	I	I	Partially soluble, splinters, air bubbles	Partially soluble, splinters, air bubbles	226.9	1.5	275.5	10.4
A4	Swells	I	I	I	I	Partially soluble, splinters, air bubbles	Partially soluble, splinters, air bubbles	228.6	1.5	254.0	8.3
A5	Swells	I	I	I	I	Partially soluble, splinters, air bubbles	Partially soluble, splinters, air bubbles	233.4	2.0	267.3	2.3
P1	I	S	I	I	I	S	Soluble, gels	162.6	1.7	169.7	1.9
P2	I	S	I	I	I	S	Soluble, gels	163.1	1.6	169.5	1.2
P3	I	S	I	I	I	S	Soluble, gels	162.8	1.7	169.2	1.2
P4	I	S	I	I	I	S	Soluble, gels	158.9	1.5	166.8	1.3
P5	I	S	I	I	I	S	Soluble, gels	157.3	1.9	166.0	1.4
P6	I	S	I	Slightly soluble (swelled, frayed & appeared textured)	I	S	Soluble, gels	161.0	1.8	168.5	1.3
P7	I	S	I	Slightly soluble (swelled, frayed & appeared textured)	I	S	Soluble, gels	158.7	3.0	167.1	2.1
V1	I	I	I	I	I	S	Swells 2x	does not melt @ 300°C			
V2	I	I	I	I	I	S	Swells 2x	does not melt @ 300°C			
V3	I	I	I	I	I	S	Swells 2x	does not melt @ 300°C			
V4	I	I	I	I	I	S	Swells 2x	does not melt @ 300°C			
V5	I	I	I	I	I	S	Swells 2x	does not melt @ 300°C			

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Table 4

Fiber	Composition	week 2 (redo)	week 4 (redo)	week 6 (redo)	week 8 (redo)	week 8	week 16	week 24	week 32	week 40	week 48
V1 fresh	100% viscose	present, some macerated	beat up, but present	beat up, but present	beat up, but present	beat up, but present	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V1 salt		present, some macerated	beat up, but present	beat up, but present	no swatch remains	beat up, but present (fiber swatch curled up, possibly protecting some fibers)	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V1 comp		present, debris adhering	present, some macerated	present, some macerated. Swatch nearly disintegrated; some bits still cling to grommet.	present, some macerated. Swatch nearly disintegrated; some bits still cling to grommet.	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V4 fresh	92% viscose, 8% spandex	present, some macerated	present, some macerated	beat up, but present	beat up, but present	beat up, but present	very beat up, but present	very beat up, but present	very beat up, but present	very beat up, but present	no recognizable fibers
V4 salt		present, some macerated	present, some macerated	beat up, but present	beat up, but present	beat up, but present	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V4 comp		fibers look fine, typcial longitudinal striations	present, some macerated	present, some macerated	beat up, but present	beat up, but present	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V5 fresh	70% viscose, 25% cotton, 5% spandex	present, some macerated	present, some macerated	beat up, but present	beat up, but present	beat up, but present	beat up, but present	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V5 salt		present, some macerated	present, some macerated	beat up, but present	very beat up, but present	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V5 comp		fibers look fine, typcial longitudinal striations	present, some macerated	present, some macerated	beat up, but present	beat up, but present	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V3 fresh	34% viscose, 63% polyester, 3& spandex	beat up, but present	beat up, but present	very macerated	very macerated	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V3 salt		beat up, but present	very few fibers, and they are beat up	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V3 comp		debris adhering; fibers a little worn but still largely intact	fibers very rare	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V2 fresh	15% viscose, 59% silk, 26% nylon	present, some macerated	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V2 salt		beat up, but present	very few fibers, and they are beat up	very few fibers, only found in one (of many) slide preps	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers
V2 comp		Fibers very macerated, and rare in preps	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers	no recognizable fibers

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