Environmentally Friendly Forensics: The Characterization of Eco-Fibers

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Abstract

Eco-fibers are now a growing sector in the fabric and textile industry. They claim to be the next step in moving towards a healthier, sustainable global environment. Eco-fibers are currently being used in the manufacturing of clothing, footwear, handbags, toys, pillows, beddings, carpets, furnishings, and many other every day products. As a result of this world wide green movement, it is inevitable that eco-fibers will come across the lab bench of trace evidence examiners. In addition, eco-fibers are becoming the fabric choice of conscientious consumers, and as a result a method must be developed for the identification of counterfeits such as those selling cotton under the guise of organic cotton.

Eco-fibers are the raw materials used to manufacture textiles without using pesticides, harmful chemicals, or synthetic fertilizers. They are resistant to mold and mildew, are free from disease and many are considered hypo-allergenic. There are several types of eco-fibers that are commercially available. Many of these are what are referred to as natural fibers replacing the man made synthetic ones; eco-fibers are those not treated with pesticides or other chemicals in growing and cultivating. Recycled synthetic fibers and synthetic fibers produced or processed using green chemistry and clean state-of-the-art technology are also classified as eco-fibers. Examples of eco-fibers are bamboo, hemp, flax (linen), seaweed, corn, soy, and even recycled polyethylene terephthalic acid, along with the more commonly used organic cotton, organic wool and silk.

Although the forensic characterization of eco-fibers has begun, there is no large scale collection of microscopical, spectrophotometric, or chromatographic data of eco-materials.

This research focuses on the collection, analysis and characterization of several different eco-fibers. The chemical characterization of these eco-fibers will be completed by polarized light microscopy, micro-melting point analysis, chemical staining, microscopical IR spectrophotometric analysis, micro-attenuated total reflection Fourier Transform (FT) IR spectroscopy, FT Raman spectrometry, and pyrolysis-gas chromatography-mass spectrometry. The best discriminatory method and combination of methods for the characterization and differentiation of eco-fibers will be determined.

The Fibers

Twenty-five eco-fibers were collected from various manufacturers: 5 bamboo, 3 corn (polylactic acid from dextrose in corn starch), 2 azlon from soybeans, 1 azlon from milk casein, 2 lyocell from seaweed, 1 recycled polyethylene terephthalate (PET), 5 organic cotton, 4 organic linen, and 2 organic wool fibers. The name, type and source/ manufacturer of the fibers are detailed in the following table.

Type of Fiber	Name of Fiber	Source/Manufacturer
Bamboo Fiber	Bamboo Rayon	South West Trading Co (SWTC)
	Black Diamond/Bamboo Carbon Fiber	South West Trading Co (SWTC)
	BMDM01	Pickering International, Inc.
	BMFL01	Pickering International, Inc.
	Bamboo	Alchemy Yarns of Transformation
Corn (Polylactic Acid) Fiber	Corn Fiber	South West Trading Co (SWTC)
	Ingeo (Corn Fiber)	Natureworks LLC
	Amaizing	South West Trading Co (SWTC)
Azlon from Soybeans	Soysilk (natural)	South West Trading Co (SWTC)
	Soysilk (white)	South West Trading Co (SWTC)
Azlon from Milk Casein	Silk Latte	South West Trading Co (SWTC)
Lyocell from Seaweed	SeaCell pure	Smartfiber AG
	Smartcel clima	Smartfiber AG
Recycled PET	Beaulieu "Green Carpet"	Beaulieu of America/Empire Carpet
Organic Cotton	OCFL01	Pickering International, Inc.
	OCFT01	Pickering International, Inc.
	Sprout	Classic Elite Yarns
	Tahki Palma	Tahki Stacy Charles
	Rowen Purelife	Westminster Fibers - Nashua
Organic Linen	ORLN01 (natural)	Pickering International, Inc.
	ORLN01 (black)	Pickering International, Inc.
	ORLN01 (beige)	Pickering International, Inc.
	ORLN03	Pickering International, Inc.
Organic Wool	Legacy Bulky	O-Wool Vermont Organic Fiber Co
	Legacy DK	O-Wool Vermont Organic Fiber Co

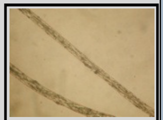
Microscopy

The morphology and optical properties of the eco-fibers were studied using an Olympus BH-2 polarized light microscope using plane polarized light, crossed polars, and crossed polars with quarter and full wave plate compensators. Optical cross sectioning was performed to determine the shape of the fibers. The eco-fibers were mounted in melt mount (n = 1.539) and in Cargille immersion oils of various refractive indices (1.440 to 1.720).

The corn fibers have the largest microscopic variation, with the Ingeo having some fibers with a spiral element and the corn fiber (SWTC) showing a surface banding only visible when mounted in a medium with a large refractive index difference from that of the fiber.

Corn Fiber (from SWTC), in plane polarized light, mounted in n=1.720 oil, showing surface "banding".

Ingeo, in plane polarized light, mounted in melt mount (n=1.539), showing spiral element.



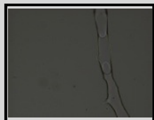
Black Diamond/Bamboo Carbon Fiber, in plane polarized light, mounted in melt mount (n=1.539).

Refractive Index

The 2 refractive indices (n), parallel ($n_{//}$) and perpendicular ($n_{\perp}$) to the fiber axis, were determined by the Becke line immersion method, using an Olympus BH-2 polarized light microscope, a 589nm filter, a temperature controlled Abbe Refractometer (Milton Roy Company), and a set of Cargille immersion oils. The isotropic n (n_{iso}) and birefringence were calculated from the $n_{//}$ and $n_{\perp}$. The error of the method was calculated to be +/- 0.0005 by propagation of error, and all $n_{//}$ and $n_{\perp}$ were rounded to the 3rd decimal, except when the 4th decimal was a 5 (represented by a subscript of 5).

Melting Point

Fibers were mounted in silicon oil with a cover glass and observed under crossed polars of a Nikon E600. Melting point ranges were determined using a calibrated METTLE TOLEDO FP82 hot stage and a FP900 Thermosystem programmed to operate from 25.0-325.0 °C, at 2.0 °C/min. The temp was recorded first when the interference colors started to change and finally when the fiber became isotropic.



Ingeo, with slightly uncrossed polarized light (5 - 10°), at 167.6 °

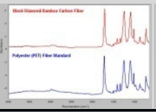
Morphology, Refractive Index, and Melting Point Table

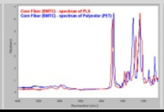
	Name of Fiber	Optical Cross Section	Morphology	Melting Point (°C)	$n_{//}$	$n_{\perp}$	n_{iso}	Birefringence
Bamboo Fiber	Bamboo Rayon	multi-lobal	few fisheyes; some fibers contain central voids	-	1.549	1.521_5	1.531	0.027
	Black Diamond/Bamboo Carbon Fiber	round	numerous fisheyes, voids and crystalline substance; // ext	-	1.672	1.538	1.583	0.134
	BMDM01	round	pockets and channels of voids; partially dyed blue; // ext except at nodes	-	1.552	1.521	1.531	0.031
	BMFL01	round	few fisheyes and voids; // ext; non-uniform light-brown/tan color	-	1.547	1.515	1.526	0.032
	Bamboo	round	variable dye uptake; // ext; pink/red color that is dichroic	-	1.549	1.514	1.526	0.035
Corn (Polylactic Acid) Fiber	Corn Fiber	round with varying diameter	intermediate central void (similar to a medula); few fisheyes, // ext.; surface "banding" when mounted in a high or low RI medium	150.2-157.1 (shrinkage started at 138.7)	1.473	1.446_5	1.455	0.027
	Ingeo (Corn Fiber)	round	scattered/few fisheyes; // ext; uniform clear color; some fibers contain spiral elements	159.3-167.6	1.472	1.444	1.453	0.028
	Amaizing	round, variable diamter, twisted	moderate voids across full diamter; // ext;	220.8-234.4	1.473	1.444	1.454	0.029
Azlon from Soybeans	Soysilk (natural)	round	numerous (heavy) fisheyes; // ext; non-uniform light-brown/tan color across fiber diameter	231.4-235.7	1.546	1.520	1.529	0.026
	Soysilk (white)	multi-lobal	intermittent fisheyes and voids; // ext; non-uniform light-brown/tan color across fiber diameter	209.2-229.9 (shrinkage started at 115.2)	1.546	1.520	1.529	0.026
Azlon from Milk Casein	Silk Latte	round	very few fisheyes; // ext; non-uniform light-brown/tan color concentrated near center of fiber	230.0-238.6	1.541	1.520	1.527	0.021
Lyocell from Seaweed	SeaCell pure	round, variable diameter, twisted	few nodes; few fisheyes; // ext except at nodes	did not melt under 325	1.555	1.519	1.531	0.036
	Smartcel clima	ribbon-like	few fisheyes; // ext; appears delustered	did not melt under 325, discolored brown at 209.9	1.523	1.520	1.521	0.003
Recycled PET	Beaulieu "Green Carpet"	trilobal	few fisheyes and voids; // ext; unifrom color across fiber	245.2-258.4	1.698	1.552	1.601	0.146
Organic Cotton	OCFL01	ribbon-like	elongated voids; undulating ext; colorless	-	1.578	1.534	1.549	0.044
	OCFT01	ribbon-like	few fisheyes; undulating ext; colorless	-	1.578	1.533	1.548	0.045
	Sprout	ribbon-like	undulating ext; dichroic clear - light green	-	1.577	1.533	1.548	0.044
	Tahki Palma	ribbon-like	nodes; undulating ext except at nodes; dichroic Lt green - clear	-	1.577	1.532_5	1.547	0.045
	Rowen Purelife	ribbon-like	// ext	-	1.577	1.531	1.546	0.046
Organic Linen	ORLN01 (natural)	ribbon-like	nodes; // ext except at nodes	-	1.593_5	1.529	1.551	0.065
	ORLN01 (black)	ribbon-like	nodes; // ext except at nodes; dichroic (Dk gray - Lt gray)	-	1.595	1.532	1.553	0.063
	ORLN01 (beige)	ribbon-like	nodes; // ext except at nodes; dichroic (Lt green - colorless)	-	1.595	1.531	1.552	0.064
	ORLN03	ribbon-like	nodes; // ext except at nodes; dichroic (Lt green - colorless)	-	1.594	1.532	1.553	0.062
Organic Wool	Legacy Bulky	oval	// ext	210.4-222.2	1.554	1.548	1.550	0.006
	Legacy DK	oval	// ext; cortical fusi; distal cut; proximal cut; appears to have been dyed light green	211.0-223.2	1.555	1.547	1.550	0.008

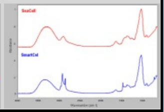
Infrared Spectroscopy

The ATR spectra were collected using an IlluminatIR™ II FTIR with a diamond ATR objective (Smiths Detection), 128 co-added scans, at 4 cm-1 spectral resolution, and a 25 µm spot size. Three of each fiber and 10 locations on each fiber were analyzed. Spectral processing consisted of averaging the 30 spectra and deleting the CO_2 and diamond lattice vibration (2400-1900 cm-1).

The IR spectra of the black diamond was consistent with PET. The spectra of the silk latte was matched to that of dry milk. The corn fiber (SWTC) was predominantly PLA, but had some locations of PET. The two seaweed lyocell fibers can be differentiated by their IR spectra.



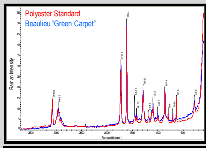


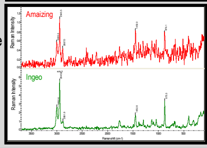


Raman Spectroscopy

The Raman spectra were collected with a Thermo Scientific NXR FT-Raman module coupled to a Nicolet 6700 FTIR, 1064 nm laser, 64 co-added scans, and 8 cm-1 resolution. The fibers were air mounted on aluminum foil wrapped microscope slides.

The majority of the eco-fibers were very weak Raman scatterers, with the exception of the Beaulieu "Green Carpet" (which was consistent with the polyester standard) and the Ingeo corn fiber. The other corn fibers were weak Raman scatterers however the major peaks of the Ingeo were present in all of the corn fibers.

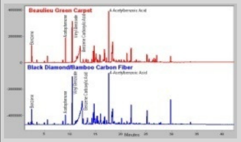


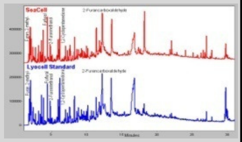


Pyrolysis GC/MS

The pyrolysis GC/MS instrument consisted of a 5150 Pyroprobe (CDS Analytical) (750 °C for 15 seconds in the pyroprobe), a 6850 GC (Agilent) w/ 5% Phenylmethyl Siloxane (HP-5MS) column (50 °C for 3 minutes, ramped to 300 °C at 8 °C/min, then 8 minute hold at 300 °C), and a 5975 MS (Agilent). The fiber sample size was 0.5 – 1.0 mg.

The chromatogram of the Lyocell SeaCell sample contained many of the same peaks present in the Lyocell standard. The Black Diamond/ Bamboo Carbon Fiber sample differed from the other bamboo fiber samples, but was consistent with the chromatogram of the 100% recycled PET sample. Comparisons of chromatograms for the bamboo fibers revealed many shared peaks with the regular and organic cotton samples.





Conclusions

This research shows the preliminary results of an ongoing study of eco-fibers. Of the 25 fibers analyzed, the black diamond/bamboo carbon fiber was shown by its refractive index, FTIR spectrum, and pyrogram to be PET, and thus counterfeit bamboo. A preliminary comparison of bamboo, recycled PET, organic cotton, organic linen, and organic wool to their non-eco counterparts (viscose rayon, polyester, cotton, linen, and wool, respectively) showed them to be indistinguishable. The melting point and morphology of the corn fibers are able to differentiate them from each other. FTIR microprobe analysis showed 1 of the corn fibers to not be homogeneous (the PLA had sections of PET mixed in). The 2 soybean azlons had different refractive indices and melting points than the previously published values, and the melting points were able to differentiate them from each other.

Further Research

- Collect more eco-fibers, of the same type and different types, and continue their characterization.
- Analyze the eco-fibers with a dispersive Raman microprobe using other lasers. Try alternative mounting methods for analysis with the FT Raman.
- Further the characterization with staining and solubility tests.
- Use chemometric analysis to further differentiate the fibers from their non-eco counterparts and to compare the different techniques ability to discriminate.

References

Bloss, D., 1961, *An Introduction to the Methods of Optical Crystallography*, New York: Holt, Rinehart and Winston.
Brinsko, K. M., 2009, *Optical Characterization of New "Eco-Friendly" Fibers,* Proceedings of the American Academy of Forensic Sciences Annual Scientific Meeting, Denver.
Challinor, J. M., 1999, Instrumental Methods Used in Fibre Examination, in Robertson, J. (ed.) and Grieve, M. (ed), *Forensic Examination of Fibres*, 2nd ed, New York: CRC Press.
Grabar, D. G. and Haessly, 1956, Identification of Synthetic Fibers by Micro Fusion Methods, *Anal. Chem.*, 28, 1586-1589.
Greaves, P. H. and Saville, B. P., 1995, *Microscopy Handbooks 32: Microscopy of Textile Fibres*, Royal Microscopical Society, New York: Taylor and Francis.
Eyring, M. B. and Gaudette, B. D., 2005, An Introduction to the Forensic Aspects of Textile Fiber Examination, in Saferstein, R. (ed.), *Forensic Science Handbook*, Vol. 2, 2nd ed, Upper Saddle River, NJ: Pearson Prentice Hall.
Keen, I. P., White, G. W. and Fredericks, P. M., 1998, Characterization of Fibers by Raman Microprobe Spectroscopy, *J Forensic Sci., 43, 82-89.*
Kirkbride, K. P. and Tungol, M. W., 1999, Infrared Microspectroscopy of Fibres, in Robertson, J. (ed.) and Grieve, M. (ed), *Forensic Examination of Fibres*, 2nd ed, New York: CRC Press.
Miller, J. V. and Bartick, E. G., 2001, Forensic Analysis of Single Fibers by Raman Spectroscopy, *Appl. Spectrosc.*, 55, 1729-1732.
Palenik, S. J., 1999, Microscopical Examination of Fibres, in Robertson, J. (ed.) and Grieve, M. (ed), *Forensic Examination of Fibres*, 2nd ed, New York: CRC Press.
Stoves, J. L., 1957, *Fibre Microscopy: Its Technique and Application*, London: National Trade Press.
The Textile Institute, 1975, *Identification of Textile Materials*, 7th ed, Manchester: The Textile Institute.
Wampler T. P. 2007, *Applied Pyrolysis Handbook*, 2nd ed, Boca Raton: CRC Press.

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