Rare Earth Emissions from Polyethylene Terephthalate Fiber

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Rare Earth Emissions from Polyethylene Terephthalate Fiber

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Joshua Jenkins Furtick
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Accepted by:
Dr. John Ballato, Committee Chair
Dr. Phil Brown
Dr. Gary Lickfield
Abstract

Rare earth-polymer blends can be useful in many applications including safety, security, displays, and novelty. Polyester, specifically polyethylene terephthalate, is a ubiquitous material in the world today and offers many opportunities for the usefulness of visible light rare earth emissions.

In this work we have attempted to incorporate rare earth complexes with polyester yarn using various methods including coating, extrusion, and dyeing, with the latter having the most success. Nanoparticles were used initially for these experiments, however certain limitations of the particles could not be overcome, for example the size of the particles and the incompatibility of the inorganic matrix with the organic yarn. A chelate complex was then synthesized. The chelate provided a smaller size for integration with the yarn, molecular compatibility with the organics, and comparable emission properties to the nanoparticles. Terephthalic acid was selected as the ligand of choice.

Methods of dyeing used for incorporation started with small scale, single strand tests. A pot dye system was used for conducting numerous simultaneous trials. A package dye system was used to incorporate the chelate complexes into entire spools of yarn. The package dyed yarn was knitted into long tubes for analysis.

The package dye proved to be a viable method for incorporation, however certain complications arose in the execution of the dyeing detailed within. Notably, a
striped pattern of discoloration similar to barré discoloration appeared in the package dyed samples. It was concluded that the discoloration is a result of the machine used, and not reflective of the efficacy of the process.

Analytical methods included elemental analysis using scanning electron microscopy and energy dispersive x-ray techniques, spectral analysis using photoluminescence, and qualitative analysis based on observations made with the samples illuminated under ultraviolet light.
Dedication

This work is dedicated to my parents, who have encouraged me to put my brain to work, study hard, and be an engineer ever since I was putting my first Lego sets together. Also to the strong women in my life who have motivated me to better myself and inspired me to push through to the end. Finally I couldn’t have done this without my brothers and the academic and familial competition they have always provided me.
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I would like to thank everyone who got me through this project, including the students in the research group: Kevin, Jonathon, Matt, Benoit, Maxime, and Colin; the summer students over the years that have helped: Vincent and Garret; and Donald Mulwee from the EM lab. A special thanks to Dr. Gary Lickfield and Dr. Phil Brown, for helping me transition from the inorganic world to the textile world.

I owe a lot of gratitude to Courtney Kucera, without whom I could never have accomplished half of what I have done here.

Finally one last thanks to Dr. John Ballato for the research opportunities that I have been granted in my time here.
# Table of Contents

Title Page ................................................................. i  
Abstract ................................................................. ii  
Dedication ................................................................. iv  
Acknowledgments ......................................................... v  
List of Tables ............................................................. viii  
List of Figures ........................................................... ix  

1 Introduction ......................................................... 1  
   1.1 Rare Earth Fluorescence .................................. 2  
   1.2 Disperse Dyeing and Polyester ....................... 9  

2 Experimental Procedures ........................................... 17  

3 Preliminary Approaches ........................................... 21  
   3.1 Nanoparticle Phase .................................. 21  
   3.2 Chelate Phase .................................... 26  

4 Chelate Analysis ..................................................... 33  
   4.1 X-ray Diffraction .................................. 33  
   4.2 Infrared Analysis .................................. 35  

5 Pot Dye Trials ......................................................... 38  
   5.1 Dyeing Methods .................................... 38  
   5.2 Results and Discussion .................................. 39  

6 Package Dye Trials ................................................... 48  
   6.1 Dyeing Methods .................................... 48  
   6.2 Results and Discussion .................................. 52  

7 Conclusions ........................................................... 58
List of Tables

6.1 The dyeing profile and machine parameters used for trials 4-7 on the Roaches Colortec package dye system .................................................. 49
6.2 The dyeing profile and machine parameters used for trials 7 and onward on the Roaches Colortec package dye system ............................ 50
6.3 Batch used for Trial 8 ........................................................................ 51
6.4 Recipe for light gray ........................................................................... 53
## List of Figures

1.1 The distribution of the worldwide production of plastics based on resin demand[15] .......................... 2
1.2 The energy level diagrams of the trivalent lanthanide ions[8] ................. 4
1.3 a. The emission spectrum of Eu$^{3+}$ and b. The emission spectrum of Tb$^{3+}$ with transitions labeled .................. 6
1.4 A schematic of a core/shell nanoparticle and the energy transfer from the shell to the core[25] ..................... 7
1.5 Various chelate molecules and structures depicted with Gd$^{3+}$ ions[30] 8
1.6 A generalized schematic of the energy transfer in rare earth chelates; radiative transitions are marked by solid arrows, nonradiative transitions are marked with undulant arrows[41] .................. 9
1.7 The synthesis process of polyethylene terephthalate from comonomers ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT), also shown is the intermediate monomer bis-(2-hydroxyethyl)terephthalate (BHET)[42] .......................... 10
1.8 a. The Atlas Laundrometer used for experimentation and b. a detail of the pots ...................................... 14
1.9 An empty package dye spool .................................. 15
1.10 Schematic of flow during a package dye cycle .................................. 16
2.1 Schematic of woven fabric with warp yarn shown in stripes and fill yarn shown in black[52] .......................... 19
3.1 Schematic of nanoparticle synthesis setup .......................... 23
3.2 a. The spool off mechanism and b. the optical draw tower used to coat fibers .................................. 24
3.3 SEM image with EDX mapping of Desolite doped with Tb:LaF$_3$ coating on polyester yarn .................................. 25
3.4 Undoped MP4 coating and MP4 coating doped with Eu:LaF$_3$ under 254 nm UV light on polyester yarn .......................... 26
3.5 An image of the chelate precipitate glowing during production, and the chelate powder glowing after processing, pictured under 254 nm UV light 28
3.6 a. The steel substrate and set up of the threads used in the proof of concept test and b. the dyed thread under 254 nm UV light demonstrating luminescence .......................................................... 30
3.7 SEM images and EDX maps showing the distribution of Eu in a chelate dyed fiber .......................................................... 31
3.8 SEM images and EDX maps showing the distribution of rare earths in a nanoparticle dyed fiber .......................................................... 32
4.1 X-ray diffraction analysis of chelate powder .......................................................... 34
4.2 Calculated x-ray diffraction patterns of terephthalic acid a. triclinic phase form I, b. triclinic phase form II, and c. monoclinic phase[58] .......................................................... 35
4.3 a. Measured ATR data for manufactured terephthalic acid powder as compared to b. the reported data for terephthalic acid[59] .......................................................... 36
4.4 Measured ATR scan of the synthesized chelate complex .......................................................... 37
5.1 Qualitative results of dyeing knitted and woven fabric with europium and terbium chelates .......................................................... 40
5.2 Pot dye results pictured under white light and 254 nm UV light .......................................................... 41
5.3 Analysis of the dye exhaustion from the pot dye trials .......................................................... 42
5.4 Qualitative analysis examining the effect of varying the amount of chelate present in the dye bath .......................................................... 43
5.5 Qualitative analysis examining the effect of varying the pH in the dye bath .......................................................... 44
5.6 Fabric used for the abrasion study, under 254 nm UV light, showing no detriment to the emissions due to abrasion .......................................................... 45
5.7 Fabric dyed with rare earth dye and traditional color dye under white light and 254 nm UV light .......................................................... 46
5.8 Qualitative analysis of difference in dye uptake of fill and warp yarn pictured under 254 nm UV light .......................................................... 47
6.1 Package dye Trial 4 under white light and 254 nm UV light .......................................................... 52
6.2 Package dye Trial 5 under 254 nm UV light dyed with chelates crushed with a mortar and pestle .......................................................... 53
6.3 Package dye spools dyed with chelate dye and traditional color dye seen under white light and 254 nm UV light .......................................................... 54
6.4 A knitted sample under 254nm UV light exhibiting the stripes characteristic of barré discoloration with the inconsistencies marked in green .......................................................... 56
6.5 A detail of the pattern of discoloration on the layers of yarn closest to the spool .......................................................... 57
Chapter 1

Introduction

The spectroscopic properties of ions from the lathanide series, often referred to as the rare earth elements, have proven useful in phospors, displays, scintillators, sensors - both optical and chemical, lasers, and amplifiers.[1–7] The specific electronic structure of the divalent and trivalent ions allows for the 4f electrons to be excitable to other energy levels.[8] The excitation of these electrons allows for the absorption and emission of photons from all across the electromagnetic spectrum, including the conversion of ultraviolet (UV) or infrared (IR) into visible light. The visible light emissions have been harnessed for LEDs, exit signs, safety, security, counterfeit detection, and novelty applications.[9, 10] The desire for polymers integrated with rare earth complexes is well-established and well-studied.[11–13] Often the desired polymers have specific optical properties that work in conjunction with the rare earth active centers, such as the clarity of poly(methyl methacrylate) (PMMA).[14] In the case of this project, the polymeric host was chosen not for its optical properties, but for the scale of its production. Polyester, and specifically polyethylene terephthalate (PET), is a ubiquitous polymer in our daily lives, showing up in packaging, plastic bottles, clothing, and other textiles. Shown in Figure 1.1, PET constituted 7% of
Figure 1.1: The distribution of the worldwide production of plastics based on resin demand[15]

the worldwide production of plastic materials in 2006.[15] The textile and PET fiber industry specifically was chosen for the scope of this project, although theoretically the proposed methods could be modified to be applied to all PET based materials. In fact similar processes have been used to label plastics to be separated for recycling.[13] The scope of this project was to devise a method of incorporating the unique spectroscopic properties of the rare earth ions into PET, and specifically the large industrial scale of the PET fiber production.

1.1 Rare Earth Fluorescence

The lanthanide series is most notable for its incomplete 4f-shell of electrons. The 4f-shell produces many relatively low lying-energy states, allowing for many easily accessible transitions.[8] An electron can be promoted from the ground state to an excited energy level by the addition of a specific quanta of energy. When the
electron drops down to a lower energy level such as the ground state there is a release of energy. The release of energy can be nonradiative, such as phonon emission or resonant energy transfer, or radiative, which can produce a photon.[16, 17] If there is a combination of radiative and nonradiative decay, there can be an absorption of energy at a particular level and the emission of a photon at a different energy level. The absorption energy can come from a photon or thermal excitation.[18] It is these types of energy conversions that make elements such as europium and terbium useful as phosphors or temperature sensors.

The energy diagrams of the trivalent lanthanide ions are presented in Figure 1.2. The accessible energy levels of an electron are controlled by the atom or ion’s environment. The atomic state, called a microstate, can be defined according to the Russel-Saunders coupling scheme. A microstate is defined by the spin (s), orbital momentum (L), and angular momentum (J); these values in this scheme are reported in the general form:[19]

\[(2s+1)L_J\]

For example the ground state of europium is the \(7F_0\) state, and a commonly populated excited state is \(5D_0\) state. Transitions such as \(5D_0\) to \(7F_2\) or to \(7F_1\) produce the photons that are characteristic of the europium(III) fluorescence. The emission spectra of europium(III) (Eu\(^{3+}\)) and terbium(III) (Tb\(^{3+}\)) ions are shown in Figure 1.3, as recorded on a Jobin Yvon Fluorolog 3 spectrofluorometer, labeled with the transitions that correspond to the emissions. The largest peaks for each of the elements fall neatly into the visible range, producing a red color from the europium and a green color from the terbium. The visible light emissions are what make these two elements particularly useful as phosphors, but as is shown in Figure 1.2, the series of
Figure 1.2: The energy level diagrams of the trivalent lanthanide ions[8]
rare earth ions can be utilized to produce emissions with many varying energies.

Traditionally the best way to harness and control these emissions was by doping the desired rare earth ion into a crystal structure, such as a ceramic for scintillation or a nanoparticle for light amplification.[3, 20, 21] A relatively low concentration of the active rare earth ions doped into a host material can be used to control the quenching of emissions by controlling the distance between the ions.[7, 22, 23] The nature of the lattice itself can also provide benefits, such as with rare earth fluorides, the lattice is more likely to allow multiphoton or cascade emissions.[24] In the case of nanoparticles, complex structures such as core/shell particles can be used to control emissions even further by way of reducing nonradiative pathways. A schematic of such a core/shell particle and its energy transfer is shown in Figure 1.4.[25] However, as is discussed in Chapter 3, it became of use for this project to examine rare earth materials consisting of an organic structure.

1.1.1 Organic Rare Earth Complexes

Instead of being hosted in an inorganic lattice, the rare earth ion can be ionically bonded directly to organic molecules. These bonds can take different forms, such as an ionic salt or a chelate structure.[26] A chelate is composed of a metal cation bonded to partners that share more than one coordination site.[27, 28] Examples of the chelate structure are depicted in Figure 1.5. Notice the organic component distributing the 3+ charge of the cation across multiple bonded sites per organic structure. To produce luminescence in either the salt or the chelate, there needs to be a particular energy transfer. The environment can vary significantly between the two proposed structures, causing different paths of energy transfer, however similar emission intensities can be observed.[29] The scope of this project will focus on the
Figure 1.3: a. The emission spectrum of Eu$^{3+}$ and b. The emission spectrum of Tb$^{3+}$ with transitions labeled.
Much work has been put into the study and characterization of the chelates of rare earth elements. The organic ligand can be considered to act as an antenna, increasing the absorption cross section, allowing for more excitation wavelengths.[31–34] The schematic for the energy transfer in a chelate is depicted in Figure 1.6, although other mechanisms have been proposed.[35] The triplet state in particular plays an important role in the transfer of energy.[29] In the specific case of terephthalic acid complexed with europium, the benzene ring absorbs the UV light, the electron is relaxed into the triplet state of the carbonyl bond, then relaxed again into excited band of the europium.[31, 36] From there it can de-excite to the ground state, emitting a photon in the visible range. The quantum efficiencies of similar molecules have been reported as high enough to make use of these molecules for light conversion.[37] The decay times for similar molecules have also been studied, with values reported from microseconds to milliseconds, proving them to be useful for displays and similar technologies.[6, 18, 38–40]

In this project, luminescent chelate molecules have been utilized for their molecular properties as well as their effective emission properties.
Figure 1.5: Various chelate molecules and structures depicted with Gd$^{3+}$ ions[30]
1.2 Disperse Dyeing and Polyester

Disperse dyeing for polyester and acetate fibers represent around 16% of the market share of dyes.[27] First synthesized in the early 1940’s under the name terylene (ICI), polyethylene terephthalate (PET) is an entirely synthetic polymer fiber.[43] One of the simplest of polyesters, PET is generally synthesized from the polymerization of monomers ethylene glycol and terephthalic acid (although other monomers are possible), a schematic of which can be seen in Figure 1.7. Like most polymers, PET is composed of both crystalline and amorphous regions.[44] The chains are held together primarily through dipole-dipole and van der Waals secondary bonding, leading to a fairly stable structure.[45] Two models have been proposed for the penetration of dye molecules into polymeric fibers, the pore model and the free-volume model. The pore model posits that dyeing can only take place by the dyeing molecules penetrating wa-

Figure 1.6: A generalized schematic of the energy transfer in rare earth chelates; radiative transitions are marked by solid arrows, nonradiative transitions are marked with undulant arrows[41]
Figure 1.7: The synthesis process of polyethylene terephthalate from comonomers ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT), also shown is the intermediate monomer bis-(2-hydroxyethyl)-terephthalate (BHET)[42]
ter filled pores scattered throughout the polymer fiber. The free-volume model states that the water and the dye molecules penetrate throughout the entirety of the free volume of the fiber.[27] Empirical evidence indicates that the free volume model is more accurate for polyesters.[27] However, small molecule diffusion experiments have shown that diffusive molecules cannot access the entirety of the free volume of PET.[46] To access the free volume (or the pores) of the PET fibers, the amorphous structure of the fiber needs to be opened through the increase of temperature; additives such as carrier molecules can also be made to help penetrate the polymeric structure.[47] The temperature at which the dye sites are found to be accessible is called the dye transition temperature, or \( T_d \), which is defined at the glass-transition temperature measured in water, not to be confused with \( T_g \) which is the glass-transition temperature of the polymeric solid.[27] For polyester dyeing, the effective dye temperature has been found to be as high as 130\(^\circ\)C. At such temperatures the dye molecules have been demonstrated to be mobile and able to migrate throughout the fiber for a more even distribution.[48]

The hydrophobic properties of the PET chain led to difficulty finding dyes that could penetrate fibers from an aqueous bath; initially only disperse dyes were able to be used successfully.[47] Disperse dyes are a class of dye that are all but insoluble in water.[27] The suspensions of such dyes were originally developed for cellulose acetate fibers, but now are also used for synthetic fibers such as PET and nylon because of their high hydrophobicity.[47] Many categories of disperse dyes exist based on chemical structures such as azo, carbonyl, or sulphur type.[27] Ignoring the effects of a dispersing agent, the equilibrium equation of a fiber in a dye bath with disperse dye can be written as such:

\[
[Dye]_{\text{dispersed}} \rightleftharpoons [Dye]_{\text{surface}} \rightleftharpoons [Dye]_{\text{fiber}}
\]
The substantivity of the dye molecule to the fiber should be high enough that the rate limiting step is the dispersion and dissolution of the solid. In order to prevent the dispersion from slowing down the exchange, the dye should be ground into adequately fine particles.[47] Common additives to the polyester dye process include wetting agents, levelers, acids, defoamers, and UV inhibitors. The wetting agent is a surfactant used to improve the dispersion of the dye. The defoamer will help prevent the dye liquor from bubbling and foaming. The acid lowers the pH to help disperse the dye and prevent hydrolysis of the dye molecules. The UV inhibitor is a chemical designed to absorb and disperse UV rays that could be harmful and cause degradation of the colorant. Levelers are molecules designed to modify the rate of exchange of the dye into the fiber. The control of the rate of exchange helps mitigate dyestrike, a process where the dye is concentrated in localized sites of the fiber. The leveler will occupy the more easily accessible dye sites, preventing a buildup of dye. As the temperature of the bath continues to increase, the leveler will be gradually rejected from the sites, allowing for a more even and level dyeing of the fiber.[47] There exist many different techniques for dyeing of polyester and dyeing in general, however for this project will only discuss the techniques useful for experimentation.

1.2.1 Specialty Dyeing Techniques

In this project two noteworthy methods of dyeing from industry have been selected for use at the laboratory or pilot scale of production: pot dye and package dye. Contrary to the desired traits of most mass production, these specialty dyeing methods have been chosen for the relatively small output and the use of non-continuous, batch method of production. This allows for the ability to conduct more trials, experiments, and changes to the system.
The first production method to be examined is called pot dyeing. Pot dyeing is a simple technique that hearkens back to the earliest days of dyeing in human history, notably similar to techniques described by Pliny the Elder and his techniques for dyeing with Royal Purple.[49] In modern practices, the process is performed with capped metal canisters, or dye pots, pictured in Figure 1.8b. The lids of these canisters make use of both a silicone pad and a Teflon seal. When used in the lid of the dye pot, the pad and seal allow the canister to become a pressure vessel, and the system is able to achieve water held in the liquid phase at temperatures much higher than its boiling point at standard atmospheric pressure. Sealed in the dye pot would be the fiber for dyeing, the dye itself, and any other chemicals necessary to the dye process including water acting as a fluid phase for the dye suspension. The fiber to be dyed in the pot can be knitted or woven into a swatch of fabric, or left as loose fiber. The dye pots are then placed into a machine called a laundrometer, pictured in Figure 1.8a. The laundrometer contains a bath of ethylene glycol to allow for the heating of the pots to a temperature appropriate for dyeing, generally above the boiling point for water at atmospheric pressure. The machine then heats up the dye pots to an optimal temperature for dyeing, while slowly rotating the pots on a radial axis to ensure even heating and also to agitate the suspensions within the pots. Once the system has been held at the dyeing temperature for the predetermined amount of time, the machine is cooled down to room temperature.

The advantages of this system include a relatively simple set up and execution. The laundrometer has capacity for multiple pots, often as many as 20-25, allowing for the simultaneous execution of as many trials, and the waste water is contained completely. The drawbacks to this system also lie in its simplicity. The sealed pots do not allow for further additions during the course of the heating and dyeing profile. Quantity of the final product is also limited. Loose fiber will end up tangled, and the
limited size of the knit or woven fabric will have limited applications. The benefits and limitations to the pot dye system all indicate that this system is ideal for early investigations with lots of trials.

The other technique utilized for experimentation is called package dyeing. Whether on the industrial scale, dyeing hundreds of pounds of fiber, or the lab scale, dyeing a few grams of fiber, the process is essentially the same. The name "package dye" refers to a package, or spool, of fiber that is to be dyed. The spool the fiber is wound onto, pictured empty in Figure 1.9, is perforated and made of a flexible plastic to allow for the swelling of the fiber; the spool pictured is provided by Mariplast. The spool to be dyed is attached on a spindle and placed into a pressure chamber that is the dyeing vessel. Water is then cycled through the vessel, passing through the spool in two possible directions alternatively, depending on the process. Illustrated in Figure 1.10, in one direction the water is forced from the spindle, through the spool, and out through the fiber into the vessel; in the other direction, the water is forced from the vessel, through the fiber and spool, and collected back into the
As the water heats up approaching the dyeing temperature of the fiber, the constituents for the dye liquor are added to the system via mechanisms such as a transfer valve or dosing pump depending on the requirements of the process. Once the cycle has run its course, the chamber can be drained, and is often followed by one or more rinse cycles. The rinse step is designed to remove any excess dye or other dye components left after the process. Polyester also has characteristic oligomers, often trimers specifically, that buildup through the course of the dyeing process that rinsing will help to remove.

The use of these techniques and how they have been applied to this project will be discussed in Chapters 5 and 6, respectively.
Figure 1.10: A schematic detailing the possible directions of flow during a package dye cycle[51]
Chapter 2

Experimental Procedures

The procedures for the incorporation of rare earths into the fiber will be discussed in the Chapters 3, 5, and 6, however some of the common experimental procedures used in all of those chapters will be discussed here.

Multiple types of yarn were provided for testing with the incorporation of the rare earth complexes. While the specific synthesis procedures and properties of each yarn are protected intellectual property, the types of yarn used can be classified by the surface characteristics and processing temperatures. The tests began with a yarn that was both textured and finished, referred to here as the finished yarn. The finished yarn was provided in both 4- and 96- filament constructions. Warp and fill yarn were tested to reproduce the characteristics of woven fabric. Woven fabric consists of two sets of yarn that run perpendicular to each other.[52] The warp yarn runs lengthwise, and generally has the smoother surface finish and the higher processing temperature. Fill yarn runs in the other direction and has a lower processing temperature than the warp yarn. The final yarn tested was an air textured yarn. Air texturing is a process that involves feeding the yarn through an air jet. The process randomly separates filaments into loops and arcs, increasing the accessible surface area in the
The standard technique used for crushing powders in this work was a modified ball milling technique. The ball milling was performed by placing 5.0 mm yttria-stabilized zirconia (YSZ) grinding media (Inframat Advanced Materials 4039GM-S050) in a polypropylene centrifuge tube (VWR Flat Cap Centrifuge Tube 50mL) with the powder. The powder and grinding media were then agitated using a vortex mixer (VWR Standard Heavy-Duty Vortex Mixer) until a fine powder was achieved.

Vacuum and vacuum oven drying were performed with Fisher Scientific Isotemp Model 281A Vacuum Oven set to 20in.Hg.

Ethanol was sourced from Pharmco-Aaper, 200 proof. Water was purified through a Barnstead Nanopure Diamond system set to 18.2 MΩ*cm to achieve so-called ultrapure water.

Microscopic analysis was performed using the Hitachi SU 6600 Scanning Electron Microscope (SEM). The voltage used for analysis was generally 1-2 keV. Elemental analysis was performed using the Energy Dispersive X-ray (EDX) attachment to the microscope. Yarn was prepared for microscopic analysis using liquid nitrogen provided by Airgas to embrittle and then cut. The yarn were prepared this way to prevent smearing or flattening so that an accurate cross section could be analyzed.

Photoluminescence (PL) measurements were performed using a Jobin Yvon Fluorolog 3 spectrofluorometer. Europoium emissions were measured with an excitation wavelength of 394 nm, and terbium emissions were measured with an excitation of 375 nm.

Qualitative evaluation of emissions was performed using a UVGL-58 Handheld UV Lamp provided by UVP. The lamp provides both 254 nm and 365 nm illumination. Pictures were captured with the use of a Zeikos 58 mm UV camera filter.

X-ray diffraction (XRD) analysis was performed using a Scintag XDS 4000
Figure 2.1: Schematic of woven fabric with warp yarn shown in stripes and fill yarn shown in black[52]
using CuK$_\alpha$ radiation. The analysis was performed on powders crushed using the ball mill technique described above.

Infrared analysis was performed by Fourier transform infrared spectroscopy (FTIR) attenuated total reflection (ATR) using a Thermoscientific Nicolet 6700 FTIR with ATR accessory. A diamond crystal was used as the substrate for the ATR technique.

Some chemicals mentioned have their names redacted to protect the intellectual property of the collaborators of this project. Other experimental methods will be discussed where appropriate.
Chapter 3

Preliminary Approaches

3.1 Nanoparticle Phase

To achieve the requisite emissions, doped nanoparticles were initially selected as the rare earth compound for use due to the stable emissions and tunable surface characteristics.

3.1.1 Nanoparticle Synthesis

Rare earth doped nanoparticles were synthesized using a lanthanum fluoride host material with an organic ligand providing absorption effects and easier incorporation into the final matrix. The rare earth dopants selected as candidates were europium (Eu) and terbium (Tb), due to their well-known emission characteristics in the ultra violet (UV) spectrum and difference in color. The synthesis of these particles, detailed in Figure 3.1, start with the rare earth solution composed of the rare earth nitrate and the host material nitrate in water that is then added dropwise to ligand/fluorine solution, which is composed of the fluorine provider and the organic ligand in water. For these particles, europium nitrate (Eu(NO$_3$)$_3$, Alfa Aesar 99.9%)
or terbium nitrate (Tb(NO$_3$)$_3$, Alfa Aesar 99.9%) were used with lanthanum nitrate (La(NO$_3$)$_3$, Aldrich 99.99%) for the rare earth solution. For the ligand/fluorine solution, ammonium fluoride (NH$_4$F, Fisher 100.0%) was used, and the organic ligand used varied. Many ligands were used in the processing of these particles as the host material and the rare earth changed, including acetylsalicylic acid (MP Biomedicals, LLC 90-100%), 3,4-dimethoxybenzoic acid (Acros 99%), phthalic acid (Fisher 99%), terephthalic acid (TCI 99%), and citric acid (Fisher 99%). The pH was measured using a VWR SympHony H10P meter. The pH was adjusted using ammonium hydroxide (NH$_4$OH, Aldrich 28% NH$_3$ in water, 99.99% metals basis), which will act as the reaction mechanism to ionize the NH$_4$F and the ligand, allowing the host material with the rare earth ion to form once added to the solution. The pH was then adjusted to 5 to keep the ligand in the final product from cross-linking and forming a gel. The combined solution stirred for one hour at 70°C in a hot bath. The particles were then separated by centrifuging the solution for 5 minutes (Damon/IEC Division CU 5000 Centrifuge). The supernatant was then poured off and the particles were washed to remove any unnecessary residual ions left from the synthesis. The washing steps included one wash with water to remove any water soluble constituents left behind, and then one wash with ethanol to help separate the particles to lessen agglomeration. The particles were then dried overnight under vacuum over a desiccant (Indicating Drierite, W.A. Hammond, 98% CaSO$_4$, 2% CoCl$_2$).

3.1.2 Coating Yarn

The first method attempted to rare earth integration into PET was to coat polyester yarn with a rare earth doped nanoparticle coating. Utilizing existing equipment for drawing glass fiber, polymer fiber was spooled down the Clemson University
research optical fiber draw tower, through a split die coating applicator manufactured by Sancliffe. A schematic of the spool constructed for this use and the draw tower are presented in Figure 3.2. The coating method would allow for pre-existing yarn to be altered with the particles, rather than a process to create the yarn, such as extrusion. Altering existing yarn was an attractive option for moving into an industrial scale, as that would mean fewer changes to the processing and the properties of the yarn. The textile yarn used for experimentation on the tower was both constructs of the finished yarn. A coating was applied consisting of 5wt% nanoparticles suspended in a coating known as Desolite (DSM Desolite 3471-3-14 provided by AngstromBond). Desolite is an acrylate coating used for optical fibers to add strength to the fragile glass fibers; it cures with ultraviolet light. A Fusion UV Systems I250 unit with a F10T illuminator and a D-bulb was used for this experiment.

The coating applied to the yarn was very uneven. The Desolite coating would not wet to the surface of the polyester yarn, in part due to the spin finish of the yarn providing a poor surface for adhesion of the coating, and the wetting properties of the coating. Figure 3.3 is a scanning electron microscope (SEM) image showing the
coated yarn in one of the “beads” of coating, particles are visible on the surface. Due to the ineffectiveness of the optical Desolite coating, a coating used for textile yarn was explored.

The coating, designated MP4, is a textile coating composed of a polyester suspension in water that is used in industry. MP4 is thermally cured instead of UV cured like Desolite, and the particles stayed in suspension more effectively than with the Desolite. However, the MP4 coating created other issues. Despite the better compatibility with the polyester substrate, the coating was still uneven. Small scale tests performed by hand in the lab were able to produce viable results, seen in Figure 3.4, however larger coating attempts on the draw tower were less successful. The MP4 coating produced yarn more evenly coated than the Desolite attempts, but the polyester coating proved more difficult to cure completely. The coated yarn came out of the tower tacky and uncured as the temperature need to cure the MP4 could not
Figure 3.3: SEM image with EDX mapping of Desolite doped with Tb:LaF$_3$ coating on polyester yarn
be achieved without the yarn breaking or deforming.

From this coating method, another problem was discovered: the polyester exhibited blue emissions, most notably present in the MP4 coating, that would interfere with any green emissions from terbium. These emissions are most likely due to the presence of optical brighteners in the polyester. Europium became the main dopant used, especially for anything involving the MP4 coating. From these results, other means of incorporation of the rare earths into the system were investigated.

### 3.2 Chelate Phase

Due to the limited incorporation of the rare earth nanoparticles into the polyester, another type of material for use with the fibers was explored. In order to enhance the incorporation of the rare earth into the polyester matrix, an organic structure was formed to house the rare earth ion to create a chelate complex. For
this work, a chelate is defined as an organic ligand providing a multidentate bond to a metallic ion.\textsuperscript{[54]} A nanoparticle is by definition approximately 10-100 nm in diameter and has a host lattice that is usually an inorganic material, such as lanthanum fluoride or yttrium oxide. Despite this very small size, these particles are simply too big and incompatible to be incorporated successfully into these yarn using the methods previously discussed. Chelates, however, have eliminated the host lattice in favor of a direct bond to the ligand, and have a structure much more compatible with the polyester matrix. Diffusion experiments with complex penetrant molecules have demonstrated that polymers such as PET more readily accept molecules that demonstrate polar interactions.\textsuperscript{[55]} Properly selected chelates should be able to exploit this property, and possibly even perform hydrogen bonding with the PET chain.

3.2.1 Chelate Synthesis

Chelate production is very similar to the production of nanoparticles, with the most notable difference being that synthesis is performed at room temperature. A ligand or complexing agent such as terephthalic acid or phthalic acid is added to ultrapure water. The solution is then stirred with a magnetic stirbar as the pH is adjusted in the same manner as described in Section 3.1.1, until the optimal pH is reached and the turns clear at room temperature. The rare earth solution is added dropwise, causing the complex to form and the solution to become cloudy. Pictured in Figure 3.5a, the precipitants glow under UV light during production, which cannot be achieved during nanoparticle production. The resulting solution is allowed to stir for an hour at room temperature, then centrifuged at 3000 rpm for 5 minutes (Damon/IEC Division CU 5000 Centrifuge), and washed with a water ethanol mix. The powder is then dried under vacuum at room temperature overnight and then
The production of chelates offers some advantages over that of nanoparticles including the lower temperature synthesis, fewer components to make the final product, and higher yield per batch, meaning the scale up process will be easier to achieve in industry.

3.2.2 Extruding Fibers

PET fibers doped with the chelate complex were attempted to be extruded. A Hills Bi-Component LBS model extruder was used, with Unifi Repreve polyester chip. An extrusion temperature of 300°C was used. Many complications arose, most notably a lack of method to distribute the chelate powder evenly throughout the polymer melt. To achieve a more even distribution, a polymer chip doped with the chelates was synthesized. The material was made by doping the MP4 coating with 1% by weight of the chelate complex, and dried under vacuum at 50°C. The resulting substrate was ground into chip. The chip was added to the PET chip for the extrusion of the fiber. Fiber was unable to be produced, as the water content of...
the MP4 derived chip was too high to successfully be extruded. The temperatures for melting and extruding the PET fibers also caused the degradation of the organic components of certain chelate complexes such as the 3,4-dimethoxybenzoic acid.

3.2.3 Dyeing with Chelates

Another method was attempted to incorporate the chelate complexes into yarn using industrially friendly methods. Dyeing using the chelates was chosen for its simplicity and potential for simple integration into existing methods. There are many dyeing methods that are used already in industry to create colored polyester. From this point, the chelate was treated as a metal ion complex used in disperse dye processing to give the yarn color that would exhibit visible emissions from the rare earths.

To determine the efficacy of the new method, a small scale, proof of concept experiment was performed. Single strands of PET yarn were tied around a steel substrate, as shown in 3.6a. Four solutions were prepared with chelate suspended in ultrapure water at 0wt%, 0.5wt%, 1wt%, and 2.5wt%. The solutions were applied twice each, using a flat sponge brush directly on the upward facing section of each thread. The steel substrate was placed in the vacuum oven at 100°C for one hour. After the substrate cooled, the handheld UV light was used to reveal the effectiveness of the applied solutions. As pictured in Figure 3.6b., the strand showed luminescence throughout the entire thread, despite only being applied to one section. This proof of concept also proved that the “dye” was dispersing through the yarn to give a uniform color. The steel substrate showed UV active residue that need to be able to remove with current methods of cleaning from industry to show contamination would not occur from one dye run to another on a larger scale. The residue was able to be
Figure 3.6: a. The steel substrate and set up of the threads used in the proof of concept test and b. the dyed thread under 254 nm UV light demonstrating luminescence removed using ultrapure water and an ultrasonic bath (Aquasonic Model 150HT) for 10 minutes, demonstrating that the chelate could be cleaned off using noncontact methods and less harsh chemicals than used in industry.

The stability of the chelate dye in the yarn was also tested in water. A dyed piece of yarn, after drying in the vacuum oven, was placed in ultrapure water and removed instantaneously. Another strand was placed in the ultrapure water for 1 minute. A third strand was placed in ultrapure water in a sonicator for 1 minute. All the strands showed the same qualitative result: the chelate was stable in the polyester without a protective coating and could not be removed with water under these conditions.

The yarn was analyzed using the SEM/EDX analysis techniques detailed in Chapter 2. The microscope images, pictured in Figure 3.7 show an even distribution of europium present throughout the cross section of the fibers. For the sake of comparison, similar techniques were attempted using the nanoparticles detailed in the previous section. The SEM/EDX analysis is shown in Figure 3.8. The images show the nanoparticles remaining outside of the fiber structure. The lack of incorporation raises concerns over degradation due to effects like abrasion resistance and
Figure 3.7: SEM images and EDX maps showing the distribution of Eu in a chelate dyed fiber

wash fastness.
Figure 3.8: SEM images and EDX maps showing the distribution of rare earths in a nanoparticle dyed fiber
Chapter 4

Chelate Analysis

Various methods of analysis were performed on the synthesized chelate powder in order to understand and characterize the properties, structure, and behavior of the powder.

4.1 X-ray Diffraction

To characterize the crystallinity of the europium terephthalic acid complex in solid phase, x-ray diffraction (XRD) was performed. The resultant graph is shown in Figure 4.1. The clearly defined sharp peaks indicate regions of high crystallinity, and, conversely, the lack of broad peaks indicate a lack of amorphous regions. The Scherrer equation was used to determine crystallite size:

$$\tau = \frac{K \times \lambda}{\beta \cos \theta}$$

where $\tau$ represents the mean size of the crystalline phases; $K$ represents a dimensionless shape factor, known as the Scherrer constant, the value is generally given
as 0.9.\textsuperscript{[56]} \( \lambda \) represents the x-ray wavelength; \( \beta \) represents the full width at half maximum intensity (FWHM) of the crystalline peaks, corrected to remove the instrumental broadening, the value of the subtraction has been determined to be 0.06 for this machine; and \( \theta \) represents the Bragg angle. The calculations revealed a mean crystallite size of 64.2 nm, and ranging from 34.2 to 115.8 nm.

Terephthalic acid under room temperature conditions tends to crystallize into a triclinic phase (form I), however at higher temperatures, another triclinic phase (form II) distinct from the low temperature phase and a monoclinic phase have been submitted as possible crystallizations. \textsuperscript{[57, 58]}

The diffraction scans of crystallized terephthalic acid found in the literature are shown in Figure 4.2.\textsuperscript{[58]} Notably absent from the theoretical scans are any peaks centered at or below around 15° to correlate with the 14.7 and 15.7° peaks apparent in the scan of the synthesized chelate. It was concluded then, that the synthesized chelate molecule and its crystallite phases do not fall neatly into any of the known structures for terephthalic acid.
4.2 Infrared Analysis

Infrared analysis was performed using FTIR and ATR techniques on manufactured terephthalic acid powder and the chelate complex. The manufactured powder scan shows relative agreement with the FTIR scan found in the literature, both shown in Figure 4.3. The strong peak at 1675 cm$^{-1}$ seen in the measured scan is reported to correspond to the C=O stretch of the carboxylic acid groups.[59] This peak will be used for comparison to the synthesized complexes.

The measured scan for the chelate complex is shown in Figure 4.4. A shift has occurred in the peak associated with the C=O bond from the position in the manufactured powder scan, indicating the rare earth ion has altered that bond. The
Figure 4.3: a. Measured ATR data for manufactured terephthalic acid powder as compared to b. the reported data for terephthalic acid[59]
broad shoulder starting at around 3600 cm$^{-1}$ is thought to correspond to the O-H bond. Although it cannot be ruled out that the peak corresponding with the O-H stretch is due to water molecules in the crystal, the peak could indicate that O-H bonds remain in the structure of the terephthalic acid complex. It remains unclear exactly how many terephthalic acid molecules are associated with each ion, although there is evidence in the literature to indicate the coordination number of the Eu$^{3+}$ ions is most likely eight.[26]
Chapter 5

Pot Dye Trials

The first method of dyeing used was the pot dye method. Pot dye is used in industry, however its limited capacity hinders its use in most applications as this method is set up to dye pieces or swatches of fabric and not individual strands of yarn. The limited capacity does make it ideal for scientific trials with many unknowns.

5.1 Dyeing Methods

Two sources of yarn were used for this dyeing method: fabric woven according to industrial methods and similar yarn knit into open ended tubes called socks using a Fiber Analysis Knitter circular knitting machine. The yarn to be knitted was oiled with a standard knitting oil for lubrication in the knitting machine. The oil then had to be scoured off before dyeing could occur. The scouring process was performed with soda ash (Arm & Hammer All Natural Super Washing Soda), all natural soap (Seventh Generation Natural Dish Liquid), and ultrapure water heated to 70°C for approximately one hour. The woven fabrics contained both warp and fill yarn, whereas the knitted fabrics were prepared with each type of yarn separately.
The wetting agent used for experimentation was a bisphenol-A alkoxylate. The leveler used is a nonsilicone, anionic surfactant.

Fabric used was cut to approximately 10 g swatches. Using results from the single strand tests, the chelates were added at 1 wt% of the fabric. Initial tests used as much as 350 mL of ultrapure water. Later tests used water in an 80:1 ratio with the fabric in an attempt to improve incorporation; for 10 g fabric swatches, this meant 800 mL of water. Terbium and europium chelates were used, both chelated with terephthalic acid. The components were sealed in the pots. Mass of the entire pot systems were recorded. The pots were placed in the laundrometer, allowed to ramp up at a rate of 2°C/min to 125°C and held for an hour. Automotive antifreeze (Zerex ZXG051 G-05 Antifreeze) was used as the source of ethylene glycol for heat transmission in the machine. After the machine had been cooled to room temperature, the pots were removed from the chamber. The pots were then rinsed to remove excess ethylene glycol, and weighed again to make sure the pot stayed sealed for the entire run. The fabric was then removed, weighed, and the fabric and the residual dye solutions were collected for further analysis. The fabric was rinsed with ultrapure water in a tabletop washing machine (The Laundry Alternative Super Compact Full Automatic Washing Machine) using lukewarm water for 10 minutes to remove any lingering dye components. Excess water was first spun off using a spin dryer (The Laundry Alternative Mega Spin Dryer) and then dried completely in a vacuum oven overnight at 50°C.

5.2 Results and Discussion

The first experiment looked at the differences in dyeing with both rare earth elements and dyeing the woven and knit fabric. The dyed fabrics are pictured in
Figure 5.1: Pictured are qualitative results showing a. woven fabric and b. knitted fabric dyed with terbium (green) and europium (pink) chelates

Figure 5.1. It was evident that the europium dye provided a more level and complete dye throughout the fabric swatch. The fabrics dyed with terbium chelates show a solid residue deposited on the outside of the fabric before rinsing. With a UV light, the solid residue was demonstrated to be dye particulate that had not incorporated into the fabric.

The next trials were amended from the first with the addition of chemicals used in industrial processes, such as a leveler, a defoamer, a wetting agent, an acid, and a UV inhibitor, in an attempt to improve the incorporation of the chelate to the fabric, and to replicate industrial techniques. Acetic acid (GFS 84%) is often used in industrial processes to drive the pH down and create a more hospitable environment for the dye in the fabric. Citric acid (Fisher 99%) was also tested in place of, and in combination with, the acetic acid. Most of the industrial additives did not show any significant difference in the sorption of the dye in the fabric. The fabrics containing terbium chelates continued to show deposited chelate residue and poor incorporation into the fabric, however fabrics with brilliant green emissions were achieved, despite the depositions on the surface of the fabric, pictured in Figure 5.2. The complications with dyeing with terbium chelates have yet to be overcome, and continuing on
europium was used more exclusively.

Figure 5.2: Successful pot dye trials showing both europium and terbium emissions, pictured a. under white light and b. under 254 nm UV light

5.2.1 Dye Exhaustion

To evaluate the efficacy of the uptake of the chelate dye complex from the dye liquor, photoluminescence (PL) on the dye suspensions before and after the dyeing process. Overall the exhaustion appeared to be poor but was inconsistent. Seen in Figure 5.3 the intensity of the europium emissions are still largely present after the dyeing process. This result is substantiated by observations of significant amounts of deposited powder remaining in the dye solution at the end of the process.

5.2.2 Chelate Dye Ratio Trial

The amount of chelate per weight of the yarn was tested to prove the 1wt% limit demonstrated in the small scale experiments. Shown in Figure 5.4, the amounts tested were chosen above and below 1%. The photographs demonstrate that the fabrics lose emissions when the concentration of chelates is increased to 2%. The small scale tests demonstrated a plateau of emissions at 1%, indicating a different fundamental phenomenon at work in the pot dye system. This was observed to be a
Figure 5.3: Analysis of the dye exhaustion from the pot dye trials
result of the chemistry of the suspension, with more of the chelate dye precipitating out with the increased concentrations in the dye bath.

5.2.3 pH Trials

Another interesting result came about from the testing of the effects of acidity of the dye solution. Industrially it is accepted that the optimal dye uptake occurs in the presence of an acid to control the pH, however there is evidence in analogous systems that a buffer solution proves to be more effective.[60] Thus pot dye trials were performed under neutral conditions using both acetic acid and potassium hydroxide in equal amounts, as well as trials with increased acetic acid and trials with potassium hydroxide in the absence of acid. Seen in Figure 5.5, the neutral dye solutions proved to have better emissions than both overly acidic and overly basic conditions. However, it was inconclusive whether the buffer solution was able to improve the incorporation over the original dye recipe.
5.2.4 Abrasion Study

To test the ability of the chelate to remain in the fabric during real world use, an abrasion study was performed. The technique performed was chosen as a simulated dry Crock test, similar to AATCC Test Method 8-2013. A 50 g weight was wrapped with undyed, knitted fabric. The undyed fabric was rubbed along the chelate dyed fabric 25 and then 50 times over a distance of 3-4 cm. The handheld UV light was used to determine if the abrasion caused any damage to the emissions of the dyed fabric. Seen in Figure 5.6, the dyed fabrics showed no effects from the abrasion, but the undyed fabrics used as an abrasive did show evidence of the chelate emissions. This indicates that the chelate dye was incorporated into the fabric successfully, and would be robust enough to survive real world applications.

5.2.5 Color Trials

The rare earth ion dye structure had been proven effective on white fabric, however to be useful in industrial and real world settings, the effectiveness of the rare earth dye had to be tested in combination with traditional disperse dyes. In similar fashion as the selection of dye bath components, the color dyes were selected to be as
congruent with industrial methods as possible. This led to the use of five color dye components, yellow, orange, red, blue #1, and blue #2, in combination to recreate a beige color seen in industry.

Pot dye trials were run according to the procedure detailed above with the addition of the color components. Trials were also run attempting to dye fabric that had been delivered already beige in color. Other parameters tested were woven and knitted fabric, the presence and lack of the UV inhibitor, and the presence of acetic and/or citric acid. The chelates used for dyeing were all europium chelates, however the chelating agent was varied. Terephthalic acid was always used, however sometimes it was supplemented by citric acid, in a 50/50 ratio by weight.

Results from these tests were largely indeterminate. The beige fabric, whether the color dyes were administered simultaneously or in succession, showed poor to no emissions. In certain samples, an off-green emission appeared, that seemed to be overpowering the chelate emissions. To fully understand this phenomenon, the next trials conducted isolated each color dye component.

It was theorized that the blue color dyes would have the most detrimental effects on the emissions due to their proximity to the ultraviolet end of the spectrum.
Figure 5.7: Fabric dyed with rare earth dye and traditional color dye under a. white light and b. 254 nm UV light

Testing each color component individually revealed a different story. Shown in Figure 5.7, none of the colored dyes showed a strong emission from the rare earth, however the yellow fabric demonstrated the mysterious green emission from the beige dye that was causing the most interference. Closer examination, not possible to capture photographically, revealed europium chelate emissions in all samples except the yellow dye.

5.2.6 Fill and Warp Yarn Testing

When examining the woven fabric, there was a slight increase in emissions in the fringe of the cut edges of the fabric. It was determined that the fringes were exposing the fill yarn of the weave, whereas in this particular weave the warp yarn is what composes most of the visible surface of the fabric. In discussions with the manufacturers of the yarns, it became known that the processing temperatures and the surface characteristics of the two yarns tested were vastly different. The warp yarn had a much higher processing temperature and a smooth surface. The fill yarn exhibited a lower dyeing temperature (approximately 130°C), similar to the maximum achievable in the laundrometer, and a more textured surface. These two factors
Figure 5.8: Qualitative analysis of difference in dye uptake of fill and warp yarn pictured under 254 nm UV light

combine to allow the chelate to have a more successful integration into the fill yarn fibers, which can be seen qualitatively in Figure 5.8. The temperature of the laundrometer process was also increased up to 135°C in the following tests to be more comparable with the processing temperature of the fill yarn.
Chapter 6

Package Dye Trials

With the relative success of the pot dye trials, a new method of dyeing was necessary. The pot dye system works well dyeing fabric or loose yarn, however, it lacks the utility to dye spools of yarn that can be knitted, woven, or otherwise transformed into fabric. A process such as package dyeing is more representative of what would be used in an industrial setting.

6.1 Dyeing Methods

A Roaches Colortec machine was used for package dyeing in this experiment. The machine was filled with water and the cycle started. The complete schedule for the first set of trials is detailed in Table 6.1. The temperature for the dyeing of PET yarn needs to approach or exceed the processing temperature of the yarn, established in this case from the pot dye trials to be at 135°C, or 275°F. The cycle will flow from both inside the spool out to the chamber (I-O), and from the chamber into the inside of the spool (O-I). The values chosen for these parameters represent the maximum and minimum times allowed for the Roaches Colortec in order to try and control the
Table 6.1: The dyeing profile and machine parameters used for trials 4-7 on the Roaches Colortec package dye system

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buildup of oligamers in the PET. After cooling down to a safe temperature to drain, the rinsing process is started. The rinsing process consists of the chamber again filling with water, the water cycling through for a specified time at an elevated temperature, and then drained again.

After establishing a baseline, further testing was performed utilizing the package dye system’s ability to allow for the addition of chemicals during subsequent steps of the dye process, replicating the industry standard procedure for this type of dyeing. As the system is increasing in temperature, the wetting agent is added first. Roughly one hundred degrees Fahrenheit higher, the leveler is added in. At the highest and final temperature, the dye is added with an acid for the optimal pH. The transfer valve was used for the additions throughout the experimental trials. The dyeing profile listed in Table 6.2, details the temperatures for the additions listed in Table 6.3. Trial 8 is given as a standard example of the recipe or batch used.
Table 6.2: The dyeing profile and machine parameters used for trials 7 and onward on the Roaches Colortec package dye system

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<td>0.005</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ultrapure Water</td>
<td></td>
<td></td>
<td>330</td>
<td>3</td>
</tr>
</tbody>
</table>
6.2 Results and Discussion

A dyed spool was achieved that emitted visible light when excited with UV light, pictured in Figure 6.1. While dye integration occurred, there were small deposits of dye particulate on the outermost and innermost layers of the spool. There was also a deposit of a black particulate on the same regions of the spool. This particulate is theorized to be coming from inside the machine itself, as it sat unused for over a decade. Thus trials 3 and 4 added successive rinsing steps, listed as steps 5-8 in Table 6.1. The black particulate was able to be minimized, however the dye particulate buildup was still present.

![Figure 6.1: Package dye Trial 4 under a. white light and b. 254 nm UV light](image)

Experiments continued in an effort to reduce the dye particulate buildup by testing different crushing methods on the chelate powder. Trials were performed using an agate mortar and pestle (Walter Stern, Inc. 12-950BB), and using an improved ball mill technique. The improved technique added successive steps of different size grinding media. These techniques did not resolve the chelate deposits, however they did appear to improve integration. Seen in Figure 6.2, Trial 5 exhibits a color that is more pink than purple. From small scale tests, this correlates with a higher concentration of chelates integrated into the fiber system.
6.2.1 Color Trials

In a similar fashion to the pot dye trials with industry standard colorants, package dye trials were performed with traditional color dyes alongside the chelate dye. Having learned from the pot dye trials that the yellow component to the beige brought undesirable emissions, the color chosen for these trials was light gray. The recipe for light gray is listed in Table 6.4. The components are added in during the third addition step described above in Table 6.3.

The light gray color proved to be compatible with the chelate emissions, as seen in Figure 6.3. The color dye appears to have an influence on the color of the emissions, resulting in a more orange appearance. While the emissions of the gray

<table>
<thead>
<tr>
<th>Component</th>
<th>% of Yarn Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>0.0573</td>
</tr>
<tr>
<td>Orange</td>
<td>0.0511</td>
</tr>
<tr>
<td>Red</td>
<td>0.0295</td>
</tr>
<tr>
<td>Blue # 1</td>
<td>0.0999</td>
</tr>
</tbody>
</table>

Figure 6.2: Package dye Trial 5 under 254 nm UV light dyed with chelates crushed with a mortar and pestle
trials were not quite as strong as the emissions in the colorless trials, the gray trials did exhibit stronger emissions than any color attempted in the pot dye trials.

![Figure 6.3: Package dye spools dyed with chelate dye and traditional color dye seen under a. white light and b. 254 nm UV light](image)

6.2.2 Transfer Valve Residue

During testing, a residue was observed to be building up in the transfer valve of the Roaches Colortec package dye machine. The residue was white in color, and viscous. Fearing a buildup of chelate dye indicating an incompatibility with the dyeing process, samples were obtained for analysis. Using SEM/EDX techniques, it was determined that there were not significant enough levels of europium present to indicate the buildup was due to the chelate powder itself. Based on the appearance of the residue, the UV inhibitor was determined to be the most likely cause. As pot dye trials proved no effect of the UV inhibitor on emissions, the agent was removed from further trials to avoid more buildup.
6.2.3 Discoloration

To fully analyze the consistency of the dyed spools, the yarn was taken and knitted into long tubes, referred to as socks, on a circular knitting machine. These socks allow for qualitative analysis of dye consistency on a small scale, comparing layer to layer on the spool, and a larger scale. To compare the consistency across the entire spool, often the material used for knitting is taken from the outside of the spool, then the middle and inside, finishing with yarn from the outside again. When constructed in that order, the socks are termed OMIO samples.

The evaluation of Trials 2-5 and beyond revealed that, while the rare earth emissions were consistent from the outside to the inside, the samples revealed significant discolorations every few centimeters of knitted fabric, similar to zebra stripes, pictured in Figure 6.5. The discoloration pictured is similar to a phenomenon called barré discoloration. Barré discoloration, defined as “a continuous visual pattern of stripiness sometimes seen in the course direction of circular knits,” has many possible underlying causes.[47] Often the discoloration is a product of the fiber itself, stemming from inconsistencies in the production of the fiber. Fiber morphology was eliminated as a possible cause in this specific case based not only on the industry standard source of the yarn, but also the pot dye trials that revealed consistent coloring with the same yarn. Ruling out problems with the yarn indicates a problem with the process.

Barré discoloration can be an indication of a failure to reach equilibrium during the dye process. For the package dye system, both time and temperature can be increased in an effort to achieve equilibrium, however the increase in time and temperature brought on by the schedule detailed in Table 6.2 showed no improvement in consistency, despite being identical to an industry standard. During the investigation of the color trials, it was discovered that the same barré striping was apparent in the
Figure 6.4: A knitted sample under 254nm UV light exhibiting the stripes characteristic of barré discoloration with the inconsistencies marked in green
coloration of the traditional dyes, which proved useful for the investigation. When the spools were unwound to the most inside layers, it was discovered that the discoloration lined up with the pattern of the perforations on the plastic spool. Another possible explanation for the discoloration could be related to the tension during spooling onto the package. A technique in which a plastic replica of the yarn is created could reveal any inconsistencies in the tension of the knitted fabrics. It was concluded then that the problems were due most likely to the equipment and machine used for experimentation, and not reflective of the overall process.
Chapter 7

Conclusions

Rare earth nanoparticles were rejected in favor of rare earth organic acid complexes. The nanoparticles exhibit brilliant emissions, however the particles were found to be too large and molecularly incompatible with the polyester yarn. With the particles unable to penetrate the fiber matrix, the abrasion resistance and wash fastness would be in question. To address these difficulties, a molecular complex known as a chelate, defined as an organic ligand with a multidentate bond to a metallic ion, was synthesized without the inorganic lattice of a particle, instead binding a rare earth ion directly to the organic ligand. Terephthalic acid was determined to be the ligand of choice due to its optical properties and molecular compatibility with the polyethylene terephthalate fiber structure. The terephthalic acid and related molecules, such as phthalic acid, have a structure that allows for the absorption of the UV light by the aromatic ring, relaxation of the energy into the triplet state of the bond of the carbonyl group, relaxation of the energy into the $^5D$ state of the rare earth ion, where that energy can finally be released as visible light on transition to the ground state. Infrared analysis shows that the molecule has shifted the peaks correlating with the C=O bond, indicating that instead of making an ionic salt, the rare earth ion is likely
bound to both oxygen atoms present in the carboxylic acid group. It remains unclear exactly the number of such bonds per ion.

Coating yarn was determined to be an ineffectual method for incorporating rare earth emissions into polyester yarn due to problems creating a coating that would adhere well to the yarn, dry completely onto the yarn, and suspend the rare earth complexes in the coating in a way that would allow for an even distribution along the yarn, all without interfering with the optical properties of the rare earth ions. Coating the surface of the yarn also would raise concerns with maintaining the rare earth emissions with abrasion and fastness properties in general of the yarn.

Extrusion of the fibers was similarly determined to be unsuccessful at rare earth incorporation. An even distribution of powdered chelate complex was difficult to achieve. Attempts to suspend the complex into polyester to be ground into chip and extruded were met with problems achieving a chip dry enough to allow for extrusion. The thermal stability of the complex was also challenged by the temperatures required for polyester extrusion.

The treatment of the complex as a dye molecule proved to be an effective method of incorporation of the rare earth emissions into the polyester yarn. The elevated temperatures of the dyeing process allow for the opening of dyesites in the yarn where the complex can penetrate and be integrated. The resultant emissions of the yarn are limited by the chemistry of the complex suspension used for dyeing at lower concentrations, and the phenomenon of quenching emissions between active centers takes over at higher concentrations.

The sharing of dyesites between the rare earth complex and traditional color dyes has proven to be inconsequential. The complexes have demonstrated emissions even while coupled with high levels of traditional color dyes. However, the darker color traditional dyes do interfere with the absorption/emission process of the complex.
Other color dyes have demonstrated unexpected emissions under UV light, indicating a fundamental incompatibility in using the rare earth complex dye and these specific traditional dyes in conjunction.

The pot dye system was proven to be useful for experimentation, as it allows for multiple, contained, simultaneous trials, and uses relatively small amounts of materials. Through the use of pot dye, it was proven that the chelate dye could be distributed evenly throughout yarn and fabric at normal dyeing temperatures, dye liquor components designed to inhibit the degradation of dyes through the absorption of UV light have no apparent effect on the emissions, dye liquor components designed to improve the compatibility of the yarn to traditional dyes could be inhibiting the absorption of the chelate dye, and the pH of the suspension plays an important role in the incorporation into the yarn.

The package dyeing system was proven to be useful for other experiments, and useful for producing yarn to be knitted for analysis and characterization. The findings from the pot dye were reinforced, including the effect of traditional color dyes, however the package dye system used proved unable to produce an evenly dyed spool. The dyed spools exhibited stripes lacking dye, which is called barré discoloration. Whether this was due to time, temperature, or other constraints, the issue was never overcome. Considering the pot dye system was able to produce evenly dyed yarn, it was concluded that the issue was with the specific Roaches Colortec machine, and not the overall process. Based on the distribution of the undyed regions, the regions appear to be a function of the distribution of the perforations and plastic lattice of the spool.
Chapter 8

Future Work

The dyeing process has been demonstrated to be an effective method of incorporation of the rare earth complexes with the polyester yarn that is useful for integration with existing industrial methods, but there is still room for optimization.

The experiments detailed in this work offered an examination of incorporating rare earth complexes into a set of PET yarns and fabrics that were provided for the research detailed herein. In order to fully understand the dyeing properties of the complexes and their behavior in the dye processes, a more complete characterization of the yarns used for dyeing would be needed for a full analysis.

The level of incorporation demonstrated in the small scale has yet to be achieved in the pot dye or package dye system, indicating that there are still inefficiencies in those systems. While increasing the chelate present in the pot dye trials resulted only in more chelate precipitated in the residual solution, it is possible that the more vigorous action of the package dye could provide a higher level of integration. Chelate residue on the outside of the yarn spool, the exposed plastic of the spool itself, and the inside of the package dye chamber post dyeing indicate that the present levels of chelate are already not being fully integrated, so it would
take subtler methods than simply increasing the concentration of the chelate in the suspension to increase the uptake.

One parameter that has not yet been fully explored is the pH of the system. Pot dye trials have indicated a range of pH that provides an increased level of integration. Moving forward, a set of experiments using very closely monitored pH values for dye suspensions should provide a more specific value for the optimal uptake. Another possible method to increase the solubility of the rare earth dye complex would be a change in the synthesis. Starting from a salt such as sodium terephthalate could improve the solubility of the final product.

Further characterization of the chelate molecule could prove to be useful. While the spectral properties of the chelates are more important than the molecular structure, there is still information that could be gleaned from the structural characterization. Methods such as nuclear magnetic resonance (NMR) could reveal the environments of atoms such as carbon, allowing for a more complete structure to be determined.[61] Information gathered from such an analysis could be used to determine the exact nature of the bonds from the terephthalic acid molecule and the Eu$^{3+}$ ions.

Another question left unanswered by the current molecular structural analysis is the exact number of terephthalic acid molecules and Eu$^{3+}$ ions per structure. Not only is the number of bonds to each ion still undetermined, the number of Eu$^{3+}$ ions per complex is still unknown. The terephthalic acid molecule has two carboxylic acid groups per molecule; there is the potential for Eu$^{3+}$ ions on either side of a single molecule. A combination of NMR, FTIR, and EDX could yield answers to this question.

The final step for integration of the discussed methods into industry is of course a major increase of scale.
Bibliography


