Abstract

The goal of this project is to continue research on microencapsulated thermochromic materials, specifically to investigate their behavior under exposure to solar irradiation, temperature, humidity, and other environmental factors, with a long-term goal of creating a stable coating that can be applied to buildings roofs and walls.

Proposal Statement

Overview of Proposed Project

Research Question –
Thermochromic materials (TCMs) possess color change properties with respect to increase of temperature. TCMs often degrade under the exposure to sunlight with a wide range of wavelengths from UV to near IR. Due to this degradation, TCMs usage for potential applications such as coating exteriors of the buildings and energy storage are limited. The research question can be summarized as follows: What is the effect of different parts of solar spectrum on degradation of pure commercial and home synthesized TCM materials, and what is the difference between solar irradiation impact on unencapsulated versus microencapsulated TCM materials.

Motivation –
Understanding the mechanism and impact of solar irradiation of TCM materials is one of the most important questions that needs to be answered before commercial use of TCM coatings can be achieved. Understanding what part of the solar spectrum causes most of the damage to the TCM and choosing the right coating to prevent that part of spectrum access to TCM is vital for making a long lasting TCM coating/paint for outdoor applications.
Brief description –
Using commercial TCMs, home synthesized TCMs, and metal oxides encapsulated TCMs will be tested to determine how solar spectrum irradiation influences each type of TCMs. Wide variety of optical filters will be used to separate certain spectrum radiations (UV, Visible (with different colors), IR, NIR) and test how each part of the spectrum influences TCM materials. Additionally, all TCM materials will be put through heat and humidity testing to determine whether heat or humidity can contribute to degradation of TCM samples. Spectroscopic, and color chromatic characterizations of the pre- and post- treated samples will be carried out with UV-Vis spectrometer, FTIR spectrometer and C.I.E. Lab Space.

Research goals –
This research project will test photodegradation and environmental stability of different types of TCM materials and determine the best mechanism (coating) to protect the TCM material from harmful radiation. The overarching goal of the project is to understand what measures should be taken for TCM materials protection from environmental factors in order to create a stable TCM coating/paint for outdoor application.

SPS connections –
This project will present a vital opportunity for our newly formed chapter to facilitate better connections between student members and induct new student SPS members interested in undergraduate research. Additionally, the project will provide much needed research experience and professional skills development for the students.

### Background for Proposed Project

The technology of chromaticity in devices can be used to vary the throughput of visible light and solar energy for windows and buildings surface application. The technologies can make use of a range of chromic materials either by themselves or in combination with other encapsulants [1]. The rapid development of smart materials has encouraged researchers to explore new possibilities. The market for chromic materials is growing rapidly because of their optical, storage and color changing properties under different stimuli. Examples of such materials are thermochromic inks [2], electrochromic windows [3], and photochromic fibers [4]. Although different chromic materials change color by different stimuli, the mechanism for such changes is similar, that is, a reversible electron or ion transfer. Generally, electrons need energy to overcome a potential barrier (ΔE) to complete the transfer and this can be provided by photons, heat, or electric potential. The TC chemicals also need to be metastable for the process to be reversible [5]. Leuco dye systems contain three components: dye, developer, and long-chain solvent. Briefly, the dye interacts with the developer to form one color when the solvent is in the solid form, while upon heating and melting of the solvent, this interaction is lost, forming an alternate color. Thus, the color change of the leuco dye system is controlled by the melting or crystallization of the long-chain solvent as shown in Figure 1 [6].

Solar degradation of TCM material can happen under UV exposure, according to Nassau [7]. Encapsulation was proven to be effective at preventing UV exposure of the dye by Zhang et al. [8]. But while it has been accepted that UV light according to experiment by Karlessi and Santamouris [9] suggests that UV, while damaging to TCM might contribute less to TCM degradation than visible spectrum components of the light. Since there is no overall consensus on what the mechanism of TCM materials degradation, further research is should be accomplished to investigate TCM’s degradation behavior.
Expected Results

Most of the TCM materials in focus of this project show color transition (black to white, blue to transparent, depending on the TCM type) around 35-45 °C. The color is an important characteristic of TCM material since the desired characteristics of TCM materials are high reflection or high absorption (depending on TCM state) of the solar irradiation. More specifically the color difference between reflective and absorptive state of TCM is an important characteristic for this project. When TCM undergoes degradation, the value of color difference between reflective and absorptive states shrinks. Using that trait of TCM materials, CIE Lab colorimeter will be used to measure the extent of sample degradation.

Degraded TCM material’s crystalline structure and surface morphology will be compared to non-degraded TCM materials using Scanning Electron Microscopy, and X-ray Diffraction. Spectral absorbance of TCM samples would be measured by UV-Vis Spectrometer.

We expect to see positive impact of metal oxide coating on a lifetime of TCM material (encapsulated TCM will have longer life under sunlight and environmental conditions). Degraded unencapsulated and encapsulated TCM materials are expected to change their crystalline structure and surface morphology, but the core shell structure of encapsulated TCM should not expect any changes, and shell of encapsulated TCM should take longer to reach same degradation stage as unencapsulated TCM.
Methods, Design, and Procedures

Materials
For this project we will use commercially available and commercially polymer encapsulated black dye, blue dye, that is synthesized in house using 1-tetradecanol, crystal violet lactone (CVL) and bisphenol A (BPA), will also be used. For encapsulation of both dyes surfactant sodium dodecyl benzene sulfonate (SDBS), the precursor tetraethyl orthosilicate (TEOS) and encapsulation catalyst, ammonia, will be used.

Methods: Encapsulation
Encapsulation of the TCM dyes was covered in detail in our previous research, since we will use same encapsulation techniques the description of said techniques is omitted [11].

Photo and environmental degradation
After encapsulation TCM samples will be characterized using SEM and XRD. Then samples of encapsulated and non-encapsulated TCMs will be coated on the glass slides using Doctor Blade tool, forming thin (100-400nm) film. Slides will be made of standard size to make characterization and experiments easier to conduct and reproduce. Different types of TCM will be coated with different thicknesses and subjected to different degradation factors, solar light intensity, heat, humidity in discrete intervals 2- 4 hours each between the exposure intervals sample slides will be tested using UV-Vis and CIE Lab colorimeter to track the degradation of samples. After samples reach full degradation (or after long period of exposure, in case degradation will not be reached in reasonably short time) samples will be characterized using SEM and XRD again to gauge the effect of degradation.

Characterization
The Hitachi SU3500 is used to obtain a high-resolution scanning electron microscopy (SEM) image. The elemental analyses of both commercial dye-based, and blue dye samples are characterized by energy dispersive x-ray spectroscopy using Oxford Instrument’s EDAX detector attached to SU3500 SEM, with a working distance of 10 mm, a takeoff angle of 35° and an accelerating voltage of 15 kV. The Hitachi’s HT7800 series is a HRTEM instrument used to determine, if the encapsulation is successful because it can offer a higher resolution to allow the delineation of the sample’s surface morphology. Dynamic Light Scattering (DLS) will be run on samples to see the extent that the reaction schemes can break down large aggregates of the TCM samples using the Zetasizer Nano Series (ZS, Model: ZEN3600) DLS which is designed to measure particle size, molecular weight, and zeta potential. Fourier transform infrared spectroscopy (Agilent 630 FTIR) will be utilized to determine the chemical and bonding environment. For the FTIR experiments, an ATR cell will be used for the plain dye and core-shell powder samples placed on the diamond window and applying pressure using a screw gauge. The transmission mode will be used to collect IR signals between 400 to 4000 cm⁻¹ wavenumbers. The thermal properties of these metal oxide encapsulated TCMs will be analyzed by differential scanning calorimetry (TA Instruments, DSC 2500) and thermo-gravimetric analysis (Mettler Toledo, TGA/DSC 1 STAR® Systems). For the TGA studies, the TCM@Metal Oxide (MO) sample size of <10 mg will be heated from room temperature to 100 °C with a ramping rate of 1 °C/min under nitrogen flow of 10 mL/min. To determine the visual color change, TCM@MO and other TCMs core shell systems will be placed on white filter paper on top of a hot plate. The hot plate’s temperature will be adjusted in increments of 5 °C while the actual temperature of the samples will be determined by an infrared thermometer.
Plan for Carrying Out Proposed Project

- **Personnel:**
  - Daniil Ivannikov – SPS Member and President, Chapter 2045, Zone 6, Full Time Undergraduate Research Student, Florida Poly
  - Addam Ben-Abdallah – SPS Member and Secretary, Chapter 2045, Zone 6, Full Time Undergraduate Research Student, Florida Poly.
  - Brennan Halsey – SPS Member and Historian, Chapter 2045, Zone 6, Full Time Undergraduate Research Student, Florida Poly
  - Dr. Sesha Srinivasan – SPS Member and Zone 6 ZC, Assistant Professor of Engineering Physics, Faculty Advisor, SPS Chapter 2054, Florida Poly

- **Expertise** - Yes, Dr. Sesha Srinivasan is an expert in materials’ development and synthesis, analytical characterization studies and scientific publication preparation.

- **Undergraduate student SPS members** have been working on material synthesis and characterization under Dr. Srinivasan supervision for over a year and have sufficient experience to carry out this project.

- **Research space** - We will conduct this proposed work in the wet chemical research laboratory of Florida Polytechnic University. We have a Characterization Lab where we will execute various characterization studies such as SEM, XRD, EDS, FTIR, UV-Vis, DLS, TGA/DSC and CIE Lab. We will also collaborate with Professors and researchers from nearby R1 institution, University of South Florida, Tampa, FL.

- **Contributions of faculty advisors or the department (equipment, space, etc.)** - Faculty Advisor Dr. Sesha Srinivasan will provide their valuable time to design the project goals and define the protocols for undergraduate research studies. Equipment such as synthetic reaction glassware and characterization equipment is housed at Florida Polytechnic University. We can also use our collaborator’s research facility at Florida Poly and at the University of South Florida.

### Project Timeline

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<thead>
<tr>
<th>Tasks</th>
<th>Start Date</th>
<th>End Date</th>
<th>Milestone/Activity</th>
</tr>
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<tbody>
<tr>
<td>Task 1</td>
<td>1/1/2023</td>
<td>1/31/2023</td>
<td>Project Start, Literature survey, Purchase of chemicals and necessary equipment</td>
</tr>
<tr>
<td>Task 2</td>
<td>2/1/2023</td>
<td>3/31/2023</td>
<td>Synthesis of sufficient amount of TCM materials, and initial sample characterization.</td>
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<tr>
<td>Task 3</td>
<td>4/1/2023</td>
<td>4/31/2023</td>
<td>Set up of Testing facilities (Solar Simulator, Environmental Chamber)</td>
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<tr>
<td>Milestone 1</td>
<td>5/1/2023</td>
<td>5/31/2023</td>
<td>Continue from the previous testing completion, Interim report submission</td>
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<td>Task 4</td>
<td>6/1/2023</td>
<td>8/31/2023</td>
<td>Extensive degradation testing</td>
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<td>Task 5</td>
<td>9/1/2023</td>
<td>10/31/2023</td>
<td>Continue the extensive degradation testing and its completion, Final sample characterization</td>
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<tr>
<td>Milestone 2</td>
<td>11/1/2023</td>
<td>12/31/2023</td>
<td>Project wrap up, final data consolidation, final report submission</td>
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</table>
**Budget Justification**

**Chemicals/Solvents/Gases, Materials and Supplies:** A number of chemicals including TCM commercial dye, metal oxides such as SiO\(_2\), ZnO, and TiO\(_2\), solvents, surfactants (SDBS, CTAB), acids, and bases will be procured for the development of microencapsulated TCMs. Gases such as nitrogen and compressed air will be procured for the TGA measurements and other synthesis purposes. Supplies such as TGA pans, and accessories, weighing boats, Whatman filter paper are budgeted for the proposed research work. An amount of $1,000 is budgeted for the chemicals, materials, and supplies for the project and will be spent during the project timeline.

**Optical Filters** from Edmund Optics. These filters could be UV-cut off filter, or other visible color filters which will be applied to the solar photodegradation experiments with the TCM coatings. An amount of $500 is budgeted procuring optical filters and other related accessories.

**UV-Vis DRS (Diffuse Reflectance Spectroscopy) solid sample holder** that will be used to examine the specular reflectance and diffuse reflectance properties of plain and solar irradiated samples. Since we have in-house integrated sphere for the DRS measurements that is equipped one for thin films, and our samples solids, therefore, we would like to procure solid sample holder for this study. An amount of $500 is budgeted to procure sample holders from Agilent company.

**In-Kind Support:** Glassware, DI water, state-of-the art instruments, expert research personnel and their time (my mentor, laboratory staff and other senior researchers) will be extensively available to support this project. Our collaborator from a Research One Institution, the University of South Florida is available for technological discussions and knowledge transfer as well as use of their research facilities.

**Bibliography**


