Rare Earth Metal Doped Titanium Dioxide Upconversion Photocatalysis for Floridian Historical Building Preservation Applications

Sruthika Baviriseaty[1], Gwendolyn Martin-Apostolatos[2], Daniel Russell[3], Venkat Bhethanabotla[3], Vignesh Bhethanabotla[3]

1. C. Leon King High School; 2. Thomas Jefferson High School; 3. Chemical Engineering, University of South Florida

Abstract

A polymer consisting of a polycarbonate urethane, Idrocap 993PF, and rare earth metal doped titanium dioxide was created via hydrothermal synthesis. This polymer was then tested to observe its potential as an application for Floridian historical building preservation. Travertine stone was used as samples to test on due to its porosity being like on those of Floridian historical building structures. The coating was then tested on its static water contact angle, capability of absorbing water, and effectiveness at degrading methylene blue dye under sunlight simulation. The results obtained from this experiment support the claim that this polymer has the potential to be used in historical site preservation.

Background

In order to address the issue of heritage preservation, various treatments have been suggested. However, treatments can only be used if they fulfill a complicated list of conditions. In order to effectively restore and maintain natural stone, treatments must: clean, consolidate, adhere, seal, and protect the surface. New technologies and discoveries have been made, bringing the use of many new materials that can fulfill all the requirements need for an ideal surface consolidation treatment: good adhesion to the stone substrate, negligible color alteration, and no harmful by-products. By conducting this experiment, I hope to identify a potential coating that meets all this criterion while still maintaining the cultural significance of historical sites.

Objectives

- Apply previous research on titanium dioxide coatings to Floridian historical buildings applications
- Obtain characteristics of most effective coating through various tests
- Address how applications and experiment could be furthered and bettered

Approach

Each of the anatase powders were made via a hydrothermal synthesis. The doped samples contained rare earth metals Erbium (III) Nitrate Pentahydrate and Ytterbium (III) Nitrate Pentahydrate. The compositions of the various samples are 100% TiO_2 and 88% TiO_2 2% Er^{3+} 10% Yb^{3+} (Fig. 1). In addition, some stones were also coated with just the Idrocap 993PF, and others were coated with a mixture of manufactured TiO_2 and Idrocap 993PF. Stones with no coating were referenced as a control.

Figure 1

The coating was created while incorporating the polycarbonate urethane Idrocap 993PF with the anatase powders via sonication in a 99:1 ratio, respectively. 2.4mL of each coating was then applied evenly to the surface of 4" x 4" travertine samples.

Prior to the dye treatment, the tiles were tested on to observe how the coatings affected the water static contact angle. The tiles were placed on a KSV CAM101, a computer controlled and user programmable video based instrument designed for the measurement of static contact angles. Small amounts were dropped onto each tile via a metal syringe. The KSV CAM101 obtained pictures while the drop was applied and later exported the static contact angles of each tile.

Once the tiles had dried, they were soon covered with methylene blue dye due to it having a similar composition as pollutants ubiquitously found in the environment. Multicolor fluorescent pictures were taken of the tiles prior to placing them in sunlight stimulation for 20 hours. Pictures were taken after the stimulation was completed, and the pre and post gradients were then compared via the NIH's ImageJ program.

Some coated tiles were also tested for their water absorption capabilities. Preliminary tests were run to obtain a time interval of 3 minutes. The tiles were submerged in water and massed every 3 minutes for 15 minutes.

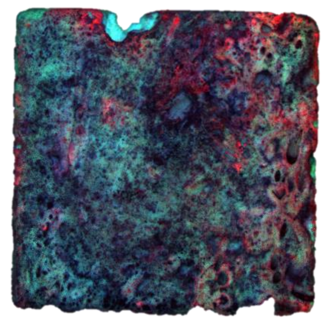

Figure 2 (No Coating)

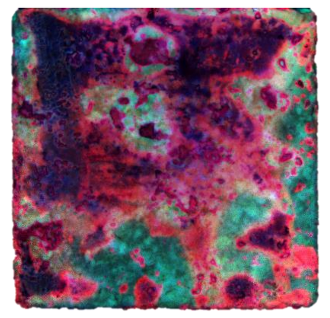

Figure 3 (Idrocap only)

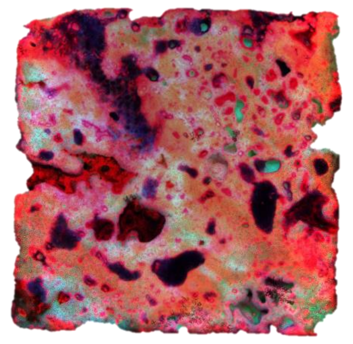

Figure 4 (TiO_2 Control)

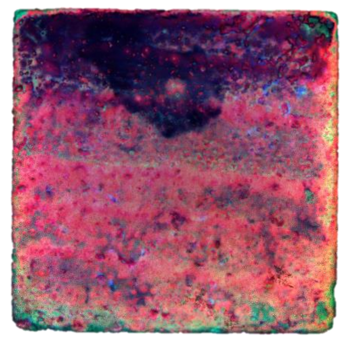

Figure 5 (Pure TiO_2)

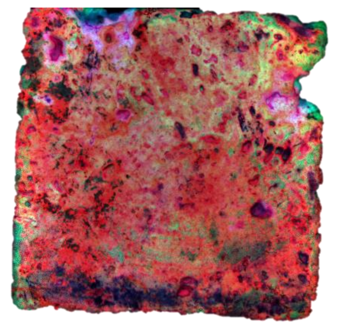

Figure 6 (10% Yb^{3+})

Conclusions

The data obtained supports the fact that the coating has the capability to be used in Floridian historical building preservation applications. This conclusion is derived from the: 1) static contact angle tests, in which the coatings were tested for their hydrophobicity/philicity; 2) water absorption tests, in which the coatings were tested on their water capillary ability; and 3) dye degradation tests (Figs. 2-6), in which the coatings were tested on how effective the polymer is at protecting the stone.

The static contact angle tests were commenced to test the wettability of the various coated surfaces. Data obtained on the tiles show that, although they all had a contact angle less then 90° (hydrophobic), the coatings had largely influenced the wettability of the travertine stone. The tiles with no coating had an average static contact angle of 24.71843°, a sharp contrast to the 73.087867° of the Idrocap only and the 75.70767° of the TiO_2 control. This demonstrates how the existence of the Idrocap played a large factor in the contact angle, whereas the titanium dioxide does not present that large of an influence.

Moreover, the water absorption tests were run on all the tiles in order to prioritize the influences of each of the coatings. The tiles with no coating absorbed an average of 1.3001 grams in 15 minutes, whereas the tiles with the 10% Yb^{3+} doped titanium dioxide absorbed only 0.189967. The addition of the rare earth metal doped titanium dioxide coating decreased the water absorption by 85%.

With the data obtained, it can be concluded that the coating is efficient at protecting porous rock such as travertine, and it could be potentially be used on various other rock found in Floridian historical buildings. My hypothesis of the 10% Yb^{3+} doped coating showing the best results is supported by the water absorption tests and could potentially be supported by further water contact angle tests. Furthermore, applications can be furthered by placing the coated tiles in natural sunlight to get more realistic results along with using different concentrations of the rare earth metals in the doped powders. By advancing this project further, information to create the best coating can be obtained and potentially applied.

Referenced Resources

1. Colangiuli, D., Calia, A., & Bianco, N. (2015). Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage. Construction And Building Materials, 93, 189-196.
2. D'Orazio, L. & Grippo, A. (2015). A water dispersed Titanium dioxide/poly(carbonate urethane) nanocomposite for protecting cultural heritage: Preparation and properties. Progress In Organic Coatings, 79, 1-7.
3. La Russa, M., Macchia, A., Ruffolo, S., De Leo, F., Barberio, M., & Barone, P. et al. (2014). Testing the antibacterial activity of doped TiO_2 for preventing biodeterioration of cultural heritage building materials. International Biodeterioration & Biodegradation, 96, 87-96.

For more information about the program visit: http://fmri-ret.eng.usf.edu/. The Research Experience for Teachers (RET) at the Functional Materials Research Institute at USF is funded by the National Science Foundation under award number 1301054.