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Enhancing the Flame Retardancy of Low Concentrations of Biodegradable Poly(vinyl alcohol) Hydrogels with Resorcinol Bis(diphenyl phosphate)

**Materials Science** 

- A. RATIONALE: Contemporarily, the world has shifted towards biodegradable, environmentally-friendly technology. Despite this, the leading fire-retardants continue to be barely-biodegradable, superabsorbent polymers. This is not only detrimental to the environment but detrimental to the users of the products as the products are not only dangerous but inefficient. The aim is to synthesize an effective, biodegradable, hydrogel made from largely organic materials that can safely protect areas of exposed skin firefighters may have when going into fires. This will prevent burns on the firefighters for longer periods of time and further research can be applied to a larger variety of situations. Regardless, the impact of fire retardant research is extensive and this project shows the superiority of modern fire retardants over conventional super-absorbent polymers.
- B. RESEARCH QUESTION(S), HYPOTHESIS(ES), ENGINEERING GOAL(S), EXPECTED OUTCOMES: What effect will the integration of RDP and starch into Poly(vinyl alcohol) based hydrogels have on the flame retardancy of said materials? How will samples respond to Thermal Gravimetric Analysis, Fourier Transform Infrared Spectroscopy, and Rheology testing? The introduction of starch coated RDP particles and the coating of the PVA hydrogel base is expected to increase the hydrogels flame retardant properties. Moreover, the best hydrogels synthesized are expected to outperform commercial super absorbent polymers employed as hydrogels. Furthermore, hydrogen bonding is expected between particles

## C. Describe the following in detail:

Procedures: To prepare the RDP-coated starch, RDP and starch will be weighed with a Mettler Toledo XPE204 analytical balance in a 3:7 weight ratio. After the mixture is placed in a 200 mL beaker and stirred with a metal spatula for 5 minutes, the beaker will be placed in a Hotpack vacuum oven for 10 minutes and kept under 40 °C. The powder will then be centrifuged three times with an ARE-250 THINKY for additional homogenization. The centrifuge spins at 750 rotations per minute (rpm) for 5 minutes and then speeds up to 2000 rpm for 10 seconds. The mixture will then be transferred back into the beaker and kept in the Hotpack vacuum oven at 60 °C for 24 hours. The RDP-coated PVA will be prepared by mixing RDP and PVA in a 1:4 weight ratio, and then heating it and centrifuging the mixture identical to the RDP-coated starch that will be prepared.

The RDP-coated PVA prepared will be separated and each sample will be mixed with different volumes of DI water to create different concentration solutions of RDP-coated PVA. Additionally, the same concentration solutions will be created with non-coated PVA and DI water. The concentrations were 1%, 2% and 4% PVA solutions in DI water, and 1%, 2% and 4% RDP-coated PVA solutions in DI water. Once these concentrations are made in 200 mL beakers, and the beakers are placed on a hot place to increase the solubility of the DI water to dissolve all of the PVA and RDP- coated PVA. After 4 hours on the hot plate, the solutions will be removed and fixed percentages of RDP and the RDP-coated starch prepared will be added while leaving one sample of each PVA and RDP-coated PVA without any addition to create a control.

These samples will be poured into petri dishes, and they will be put through a cyclic freezing and defrosting cycle to form hydrogels. The petri dishes will be placed in a freezer at -20°C for 24 hours and then taken out of the freezer to defrost at room temperature for 1 hour. They will then be placed in the freezer for another 24 hours and taken out to defrost. This cycle will be repeated once more until gel-like structures were formed.

To test the samples, each hydrogel prepared in 2.3 will be placed on a thin layer of sheepskin membrane in a 2cm x 2cm x 0.5cm aluminum tin. The sheepskin membrane will be cut to 2cm x 2cm to fit the bottom of the tin, and the gelatinized hydrogel sample is to be placed on top. A Bernzomatic Fat Boy blowtorch fueled with propane will be used to burn the gels for 3 minutes and observed how they char. Thermal Gravimetric Analysis (TGA) is a method through which the thermal degradation properties of a material are discerned. The temperature a material is exposed to is slowly increased and the deterioration of the material is observed. The test will be performed on a TGA/SDTA851 (Mettler Toledo, USA), and will be heated from 35 °C to 750 °C at a rate of 10 °C/minute under 20 mm/min nitrogen flow. We will perform Rheological studies on the samples using a Bohlin Gemini HR Nano rheometer (Malvern Instruments, UK) to determine whether each sample demonstrates shear-thickening or shear-thinning properties. Additionally, A Thermo Scientific Nicolet 6700 (Thermo Fisher Scientific, USA) Fourier-transform Infrared Spectroscopy will be utilized to characterize the presence of hydrogen bonds between the RDP and the PVA.

## Risk and Safety:

In order to ensure safety proper care needs to be taken around hazardous machines and chemicals. The TGA machine needs to be handled with caution due to its ability to reach extremely high temperatures and its slow cool-down rate. The other machines are quite delicate and so proper care needs to be taken as to not break the rheology or FTIR machines. Additionally, proper personal protective equipment must be worn at all times when handling samples and machines. This consists of gloves, lab coats, and splash goggles. Finally, care needs to be taken around chemicals like PVA and RDP in case of spills as they can cause falls and safety issues if dropped.

## Data Analysis:

To analyze data and results, all data received from the procedures described will be plotted on their own respective graphs. Then the data will be compared between samples to find the best sample in terms of flame retardancy. Additionally based on the shape of plotted curves, properties like shear-thickening/shear-thinning will be discerned about the samples. Moreover, the presence of, or lack thereof, of hydrogen bonds will be identified by graphing FTIR results. All of these graphs will be visually analyzed and conclusions drawn.

## D. BIBLIOGRAPHY

- [1] "Ultimate Biodegradation of Ingredients Used in Cleaning Agents." ScienceDirect, Elsevier Science B.V., 19 Oct. 2007, www.sciencedirect.com/science/article/pii/B9780444516640500206.
- [2] "US5087513A Flame Retardant Film and Composite Containing Superabsorbent Polymer." Google Patents , Google, patents.google.com/patent/US5087513A/en.
- [3] "Iranian Polymer Journal Home Page." Iranian Polymer Journal Home Page, journal.ippi.ac.ir/.
- [4] Cheng, Zhihan, et al. "Sustainable, Low Flammability, Mechanically-Strong Poly(Vinyl Alcohol) Aerogels." Polymers , MDPI, 5 Oct. 2018, www.ncbi.nlm.nih.gov/pmc/articles/PMC6403961/.
- [5] Bright, Danielle A., et al. "Resorcinol Bis(Diphenyl Phosphate), a Non-Halogen Flame-Retardant Additive Bright 1997 Journal of Vinyl and Additive Technology Wiley Online Library." Journal of Vinyl and Additive Technology , John Wiley & Sons, Ltd, 16 Apr. 2004, onlinelibrary.wiley.com/doi/pdf/10.1002/vnl.10184
- [6] "Improved Flame-Retardant and Tensile Properties of Thermoplastic Starch/Flax Fabric Green Composites." Carbohydrate Polymers, Elsevier, 16 Mar. 2017, www.sciencedirect.com/science/article/pii/S0144861717302928.
- [7] "Fire-Resistant Hydrogel-Fabric Laminates: A Simple Concept That May Save Lives." ACS Applied Materials & Interfaces, pubs.acs.org/doi/abs/10.1021/acsami.5b10538.
- [8] Fahy, R. F., LeBlanc, P. R., & Molis, J. L. (2017). Firefighter fatalities in the United States. Quincy, MA: NFPA.
- [9] Ma, H., & Damp; Fang, Z. (2012). Synthesis and carbonization chemistry of a phosphorous—nitrogen based intumescent flame retardant. Thermochimica Acta, 543, 130-136. doi:10.1016/j.tca. 2012.05.021
- [10] Wang, J., Ren, Q., Zheng, W., & Samp; Zhai, W. (2014). Improved Flame-Retardant Properties of Poly(lactic acid) Foams Using Starch as a Natural Charring Agent. Industrial & Samp; Engineering Chemistry Research, 53(4), 1422-1430. doi:10.1021/ie403041h
- [11] Wang, Y., Su, Q., Wang, H., Zhao, X., & Liang, S. (2018). Molded environment-friendly flame-retardant foaming material with high strength based on corn starch modified by crosslinking and grafting. Journal of Applied Polymer Science, 136(11), 47193. doi:10.1002/app.47193
- [12] M.n., P., & Song, J. (2018). Fabrication and characterisation of starch/chitosan/flax fabric green flame-retardant composites. International Journal of Biological Macromolecules, 119, 1335-1343.
- doi:10.1016/j.ijbiomac.2018.07.006
- [13] Wu, K., Hu, Y., Song, L., Lu, H., & Samp; Wang, Z. (2009). Flame Retardancy and Thermal Degradation of Intumescent Flame Retardant Starch-Based

Biodegradable Composites. Industrial & D. Engineering Chemistry Research, 48(6), 3150-3157. doi:10.1021/ie801230h [14] Shao, N., Xue, F., Hou, L., Li, D., Gao, Y., & D., Zhu, X. (2019). Effects of ternary potassium containing intumescent flame retardant coating on the combustion and thermal degradation properties of reconstituted tobacco sheet. Thermochimica Acta, 678, 178310. doi:10.1016/j.tca.2019.178310 [15] Pack, S., Kashiwagi, T., Cao, C., Korach, C. S., Lewin, M., & D., Rafailovich, M. H. (2010). Role of Surface Interactions in the Synergizing Polymer/Clay Flame Retardant Properties. Macromolecules, 43(12), 5338-5351. doi:10.1021/ma100669

[16] Christie M. Hassan, Nikolaos A. Peppas et al., "Structure and Applications of Poly(vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing/Thawing Methods" Biopolymers · PVA Hydrogels, Anionic Polymerisation Nanocomposites pp 37-65, Advances in Polymer Science", 20 October 2000, https://link.springer.com/chapter/10.1007/3-540-46414-X\_2.