Effects of Polymers on Dissipative Self-Assembly

Shaun Walters
smwalt00@umd.edu
Science, Discovery and the Universe

Research Question

In any living creature, there are chemical reactions continuously happening which are vital to sustaining life. These reactions never reach equilibrium. Understanding these out-of-equilibrium systems is a key component to understanding many of the mysteries of life. In our research, we looked at the formation and dissipation of a bovine serum albumin (BSA) based hydrogel, fueled by a redox reaction between hydrogen peroxide (H_2O_2) and dithiothreitol (DTT). We specifically look at the impact of adding polyethylene oxide (PEO) at various molecular weights on the dissipative self-assembly of the hydrogel.

Research Context

Dissipative self-assembly, out-of-equilibrium processes are more common in nature than a lab setting. These processes are vital to many different cellular processes, which use molecules, such as adenosine triphosphate (ATP), as a fuel source.[1] While difficult to replicate in a lab, out-of-equilibrium systems have a lot of potential for learning about biological systems.[2] Dissipative self-assembly in a lab works in a very similar manner to the processes found in nature, consuming a chemical fuel to create the structure.[3] We can alter various values, such as reaction rates and fuel levels, in order to change the properties of an out-of-equilibrium system, such as lifetime stiffness, and self-regeneration.[4]

Methodology

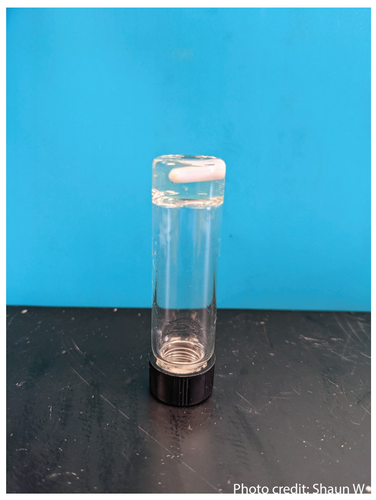
BSA was chosen for its ability to conjugate and transport molecules.[5] Protein based hydrogel also are significantly more bio-compatible and biodegradable, allowing for a safer a more sustainable experiments compared to synthetic hydrogel.[6] The goal was to understand how different concentrations of fuel impact the formation and dissipation rates of the hydrogel. We also added various levels of polyethylene oxide (PEO). The addition of a polymer was to see how it would change the mechanism of the hydrogel. Previous studies, which did not implement polymers, had relatively slow formation and dissipation rate. Our study tries to shorten an approximate twelve-hour process into a significantly shorter time frame.[7] In order to study the hydrogel, we primarily used dynamic light scattering (DLS). This involves using analyzing light scattered by a material to better understand the material's properties. Since larger particles diffuse light more, we can see an increase in the intensity of the scattered light when larger particles are being analyzed. [8] For our purposes, this is associated with the hydrogel being in a more solid, less viscous, state.[9] The process used to study began with observational analysis on many different hydrogels to see if the hydrogels successfully formed and dissipated in a reasonable amount of time. This involved adding various amounts of BSA, DTT, and PEO which were dissolved in a 6M Guanidine buffer at 5.4pH. After fully dissolved, H2O2 was added, starting the redox reaction that fuels the hydrogel. Successful hydrogels were later recreated using the same process and then analyzed using DLS. This allowed us to a more quantitative understanding of the hydrogel formation and dissipation.

Limitations

The primary limitation to our method is inconsistencies with the timing of the hydrogel preparations. The amount of time the DTT has to interact with the BSA impacts how the gel forms and dissipates. Our current timing mechanisms can sometimes does not provide enough time for the BSA to fully dissolve, while also keeping the timing consistence between tests. The DLS system also requires the sample to be mostly transparent, meaning higher concentrations of PEO were not possible as the sample became translucent.

Figures

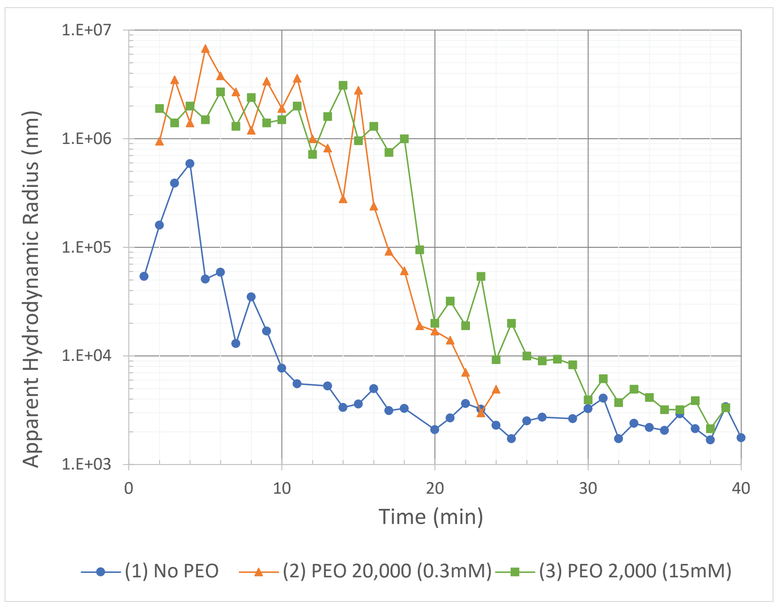
Solid Hydrogel



Melted Hydrogel

Hydrogel with PEO

Graph of Hydrogel Particular Size Overtime



Analysis

From our experiments, we saw about a 10-to-20-minute extension to the life span of the hydrogel when PEO was implemented. In graph above, we see three separate hydrogels: one without any PEO (#1 - blue), one with 0.3mM of PEO 20,0000 (#2 - orange), and one with 15mM of PEO 2,000 (#3 - green). All other variables were held constant between trails. #1 gives a base understanding of the time of dissipation. From this, we see can see both #2 and #3 have significantly longer dissipation times. While #2 does have a higher molecular weight (MW) of 20,000 g/mol, it has a concentration 50 times less than #3. #2's lower concentration is what most likely causes it to dissipate faster than #3. The PEO could be providing a sort of chemical structure to support the solid hydrogel. This structure could make the solid state more stable, enabling it to consume less chemical fuel overtime, and therefore extending its lifespan.

Future Research

Out-of-equilibrium systems and protein-based hydrogels have several reasons to further studying, such as better understanding the cell processes that enable life and possibly shortening the healing time for wounds.[10] Our paper discovered that increasing the concentration of PEO can extend the lifespan of a hydrogel. This is most likely due to the hydrogel consuming less fuel overtime. One would expect that there is a saturation concentration associated with the amount of PEO added. Future research could explore this idea and try to discover at what concentration does the addition of PEO no longer have an effect. Our research also was primarily focused on the dissipation of the hydrogel. This was due to the fact that, in the time required to align the laser, most of the hydrogel was formed. Future research could try to either slow the formation time so that this time is insignificant or use other methods of analysis. This would allow researchers to get a better understanding of the effects of PEO on the formation of the hydrogel.

Citations

(1) Gallet, F.; Arcizet, D.; Bohec, P.; Richert, A. Power Spectrum of Out-of-Equilibrium Forces in Living Cells: Amplitude and Frequency Dependence. Soft Matter 2009, 5 (15), 2947.
(2) Merindol, R.; Walther, A. Materials Learning from Life: Concepts for Active, Adaptive and Autonomous Molecular Systems. Chem. Soc. Rev. 2017, 46 (18), 5588–5619.
(3) van Rossum, S. A. P.; Tena-Solsona, M.; van Esch, J. H.; Eelkema, R.; Boekhoven, J. Dissipative Out-of-Equilibrium Assembly of Man-Made Supramolecular Materials. Chem. Soc. Rev. 2017, 46 (18), 5519–5535.
(4) Boekhoven, J.; Hendriksen, W. E.; Koper, G. J. M.; Eelkema, R.; van Esch, J. H. Transient Assembly of Active Materials Fueled by a Chemical Reaction. Science 2015, 349 (6252), 1075–1079.
(5) Majorek, K. A.; Porebski, P. J.; Dayal, A.; Zimmerman, M. D.; Jablonska, K.; Stewart, A. J.; Chruszcz, M.; Minor, W. Structural and Immunologic Characterization of Bovine, Horse, and Rabbit Serum Albumins. Mol. Immunol. 2012, 52 (3–4), 174–182.
(6) Cellulose-Based Superabsorbent Hydrogels; Mondal, M. I. H., Ed.; Springer International Publishing: Cham, 2019.
(7) Ogden, W. A.; Guan, Z. Redox Chemical-fueled Dissipative Self-assembly of Active Materials. ChemSystemsChem 2020, 2 (4). https://doi.org/10.1002/syst.201900030.
(8) Goldburg, W. I. Dynamic Light Scattering. Am. J. Phys. 1999, 67 (12), 1152–1160.
(9) Stetefeld, J.; McKenna, S. A.; Patel, T. R. Dynamic Light Scattering: A Practical Guide and Applications in Biomedical Sciences. Biophys. Rev. 2016, 8 (4), 409–427.
(10) Rohiwal, S. S.; Ellederova, Z.; Tiwari, A. P.; Alqarni, M.; Elazab, S. T.; El-Saber Batiha, G.; Pawar, S. H.; Thorat, N. D. Self-Assembly of Bovine Serum Albumin (BSA)–Dextran Bio-Nanoconjugate: Structural, Antioxidant and in Vitro Wound Healing Studies. RSC Adv. 2021, 11 (8), 4308–4317.

Acknowledgments

Special thanks to Dr. Mikhail Anisimov and Shakiba Nikfarjam for supporting and guiding my research. I'd like to thank Dr. Gottlieb Oehrlein for helping my discover my passion for research and Material Science. Thank you to all the SDU staff, especially Dr. Alan Peel and Ms. Erin Thomson. I'd also like to thank all the teachers through out my education, especially Mr. David Cox and Mr. Bill Johnstone, for piquing my curiosity. Finally, thank you to my parents for always supporting my pursuit for educational.