Polyurethane Shape Memory Polymer Foams with Off-the-Shelf Physical Blowing Agents

Natalie Marie Petryk, Anand Utpal Vakil, and Mary Beth Browning Monroe
Biomedical and Chemical Engineering, BioInspired Syracuse, Syracuse University, Syracuse, New York

Statement of Purpose: Polyurethane shape memory polymer (SMP) foams have countless biomedical applications.[1] The current synthesis of these foams for use within the biomedical field involves a 48-hour, two-part mixing process. Depending on the application, the pore size may need to be altered; the main mechanisms for pore size control are to alter premix viscosity and to utilize a chemical or physical blowing agent. Currently, our lab employs water as a chemical blowing agent through the release of carbon dioxide upon reactions between water and isocyanates. Enovate (HFC-254fa) is a physical blowing agent currently used to control for pore size and create open pores, but it is only available from a single supplier, making its use in commercial SMP foams risky. Additionally, the Environmental Protection Agency (EPA) considers Enovate unacceptable because hydroflouro-carbons are a greenhouse gas with the potential to contribute to global warming.[2] There exists a need to easily and safely modify the porosity and interconnectivity of polyurethane foams for commercial use. This work focuses on synthesizing SMP foams with readily available physical blowing agents that are approved by the EPA to find alternate options for tuning SMP foam porosity.

Methods: *Foam Synthesis:* Eight-gram polyurethane control foams were made from polyols and diisocyanates with the addition of acetone, methyl formate, or dimethyoxymethane (methylal) as physical blowing agent. An isocyanate (NCO) premix was made with 0.35 hydroxyl (OH) molar equivalents (70% hydroxypropyl ethylenediamine (HPED), 30% triethanolamine (TEA)) and 1 isocyanate (NCO) molar equivalent (hexamethylene diisocyanate (HDI)). This premix was reacted at 50°C for 48 hours. Then, surfactant was added and mixed for 30 seconds at 3500 rpm. The remaining 0.65 molar equivalents of OH (HPED and TEA) were mixed at 3500 rpm with water and catalysts (T-131 and BL-22). The hydroxyl mix and premix were then combined and mixed at 1600 rpm for 2 seconds. The physical blowing agent (0.5 mL, 1 mL, or 2 mL) was quickly added, and the solution was mixed for a final 3 seconds at 1600 rpm prior to foaming at 50°C. *Foam Characterization:* Before characterization, all foams were washed with ethanol and deionized water, then dried under vacuum for 24 hours. Differential scanning calorimetry (DSC) was run on 3-5 mg pieces from each foam to test the glass transition temperature (Tg). Scanning electron microscopy (SEM) images were taken of the foams to analyze their average pore size; ~1 cm diameter samples were taken from the top, middle, and bottom of the foams along both axial and transverse axis. To test the expansion profile of the foams, they were heated, radially crimped, and cooled. Then, crimped samples were submerged in a water bath at 37°C. Images were taken throughout the expansion process.

Results: *Foam Synthesis:* Control foams have been synthesized containing no physical blowing agent, 0.5 mL acetone, 0.5 mL and 1 mL methyl formate, and 0.5 mL and 2 mL methylal. *Foam Characterization*: SMP foams should have a dry Tg >50°C to enable stable storage in their secondary shape. The dry glass transition temperature was ≥ 50°C for all foam formulations. The foams should expand and experience shape recovery in 37°C water within 5 minutes to enable fast shape-filling after implantation. All foams expanded and demonstrated shape recovery well within 5 minutes, with most expanding completely around 40 seconds. Ideally, addition of physical blowing agents can be used to tune pore size and interconnectivity. As can be seen in **Figure 1**, the 0.5 mL and 2 mL methylal control foams had the largest pores of 1464 ± 288 µm and 1429 ± 136 µm, respectively. The 0.5 mL acetone control foam had the smallest pore size with an average of 684 ± 141 µm, which is attributed to its higher boiling point. Methyl formate did not affect pore size, but pinholes can be seen in pore walls in the methyl formate foams (SEM images in **Figure 1c** and **d**), providing an option for opening pores while maintaining overall pore size.

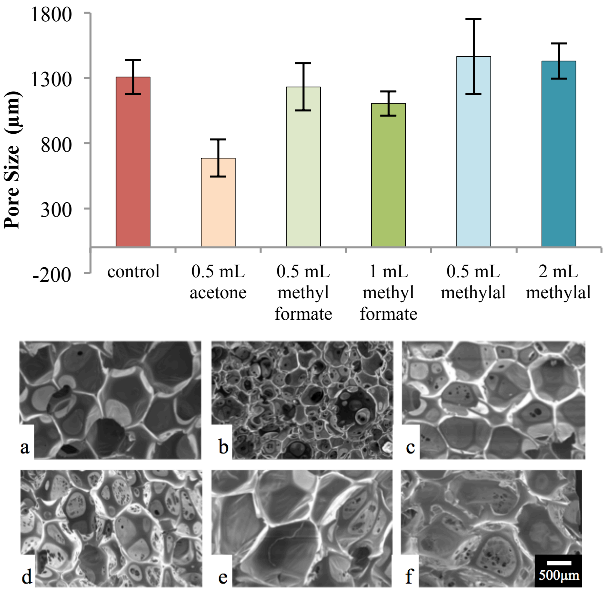

Figure 1. Average pore size of foams (top) and SEM images of pores (bottom) for a) control, b) 0.5 mL acetone, c) 0.5 mL methyl formate, d) 1 mL methyl formate, e) 0.5 mL methylal and d) 2 mL methylal.

Conclusions: The physical blowing agents impacted foam architectures in terms of pore size and connectivity, while maintaining thermal and shape memory properties. This work provides a simple method for tuning SMP foams with readily available and EPA-approved agents, which could aid in commercialization efforts.

References:

[1] Serrano, M.C. and Ameer, G.A. (2012), Recent Insights Into the Biomedical Applications of Shape memory Polymers. Macromol. Biosci., 12: 1156-1171. [2] Tsai, W.-T. (2005). An overview of environmental hazards and exposure risk of hydrofluorocarbons (HFCs). *Chemosphere*, *61*(11), 1539–1547.