

Effects of Commercially-Available Catalysts on Shape Memory Polymer Foam Properties

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Statement of Purpose: Polyurethane shape memory polymer (SMP) foams have multiple applications for wound healing, including hemorrhage control, drug delivery, and tissue engineering.¹ Polyurethane foam synthesis requires use of a blowing and a gelling catalyst. The blowing catalyst aides pore formation by facilitating the reaction between isocyanates and water to release CO₂ as a byproduct, while the gelling catalyst helps stabilize the porous structure.² Currently, our lab utilizes catalysts provided solely by Evonik: T-131 gelling catalyst and BL-22 blowing catalyst. Since these catalysts are only provided by a single supplier, they are not ideal for use in SMP foam commercialization. Should that company cease catalyst distribution, production of foams, and consequently their use as wound treatments, would be interrupted. This work evaluates readily available catalysts and their effect on foam properties, including porosity, interconnectivity, shape memory behavior, and glass transition temperature.

Methods: *Foam Synthesis:* Sixteen-gram polyurethane foams were synthesized through reaction between polyols and diisocyanates. An isocyanate premix of 0.35 hydroxyl (OH) equivalents (70% hydroxypropyl ethylenediamine (HPED), 30% triethanolamine (TEA)) and 1 isocyanate (NCO) molar equivalent (hexamethylene diisocyanate (HDI) was speed mixed for 30 seconds at 3500 rpm to thoroughly incorporate all components and then was left to react for 48 hours at 50°C. Surfactant was added to the premix and mixed at 3500 rpm for 30 seconds. In a separate container, HPED, TEA, DI water, and catalysts were combined to form the OH mix. Different combinations of gelling and blowing catalysts were incorporated (T-131 or tin(ii)ethyl hexanoate for gelling, and BL-22, DABCO, or pentamethyl diethylenetriamine (PMDTA) for blowing). The NCO and OH mixes were combined, mixed for 5 seconds at 1800 rpm, and poured into a mold to foam. *Foam Characterization:* Foams were first washed with 70% ethanol and DI water to remove any unreacted material and subsequently placed in a vacuum oven for 24 hours or until dry. Differential scanning calorimetry (DSC) was used to assess glass transition temperature (T_g) of 3 to 5 mg foam samples. Scanning electron microscopy (SEM) was used to view the porosity and interconnectivity of the foams. Images were taken of samples at the top, middle, and bottom of the foam along parallel and perpendicular axes relative to the direction of blowing. GNU Image Manipulation Program (GIMP) histogram analysis was used to quantify percent interconnectivity, and ImageJ was used to measure pore size. To test shape memory properties, cylindrical punches were cut out of the foams, heated above their T_g, radially crimped, and measured for length and average diameter. These samples were placed in a DI water bath at 37°C for 10 minutes. Measurements are again taken after the foam was removed from the bath to determine volume expansion.

Results: *Foam Synthesis:* A control foam was synthesized with both Evonik catalysts. Then, foams were synthesized by switching out only one catalyst (gelling or blowing) to understand the effect of individual catalysts, i.e., tin(ii)ethyl hexanoate as the gelling catalyst and pentamethyl diethylenetriamine (PMDTA) or DABCO as the blowing catalysts. *Foam Characterization:* All foams retained a dry T_g greater than 48°C, enabling stable storage in dry conditions. All foams experienced full volume recovery within 5 minutes at 37°C, except for the control which only recovered ~80% (**Figure 1**). Overall volume expansion increased significantly and occurred more quickly in foams with the replacement catalysts. Microscopically, there was a minimal increase in interconnectivity and pore size with the use of the new catalysts, displaying how the chosen catalysts are good substitutes to maintain overall foam structure.

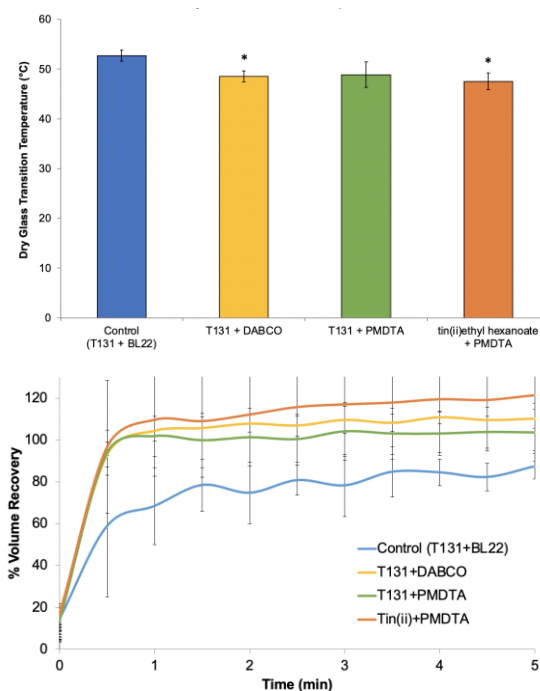


Figure 1: Dry glass transition temperature of synthesized foams (top) and expansion profile of foams (bottom).

Conclusions: Replacing the Evonik catalysts did not significantly alter overall foam synthesis protocols or resulting chemical or thermal properties relevant to foam function in wound healing, such as T_g or volume expansion. Future work includes introducing readily available physical blowing agents to tune foam pore structures, as well as exploring blood and cell interactions with these foams to ensure safety of the foams for future in vivo use.

References:

- [1] Serrano, M.C. et al. (2012), *Macromol. Biosci.*, 12: 1156-1171. [2] Dworakowska, S. et al. (2014), *Catalysis Today*, 223:148-156.