Effects of Toluene on Ionic Transport & Curing Properties of Epoxy Sealants

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DP420 epoxy samples were fabricated using various concentrations of toluene solvent to be tested under several conditions to better understand potential for ion transport as related to solvent concentration. Cube samples of 0, 10, and 20% toluene were subjected to soaking experiments where samples of high toluene concentration were found to absorb less. Differential scanning calorimetry testing of the same variations led to the identification of residual toluene in high solvent samples. It's hypothesized that ion transfer in diluted samples will be higher, but this hypothesis has not been directly tested.

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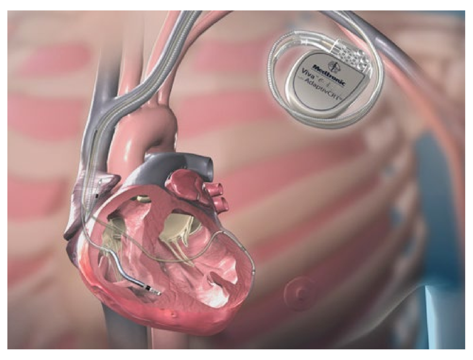
Background & Introduction

Medtronic is the global leader in healthcare technology with facilities and employees in more than 150 countries [1,2]. One of the company's main sectors is cardiac rhythm management such as pacemakers and defibrillators. The complex electrical systems housed in these devices must be properly encapsulated, calling for a material that can act as both an adhesive and a sealant. Thermoset materials, such as epoxy and silicone, are commonly chosen for this application. In this study, epoxy is employed as the external sealant that prevents ion transport.

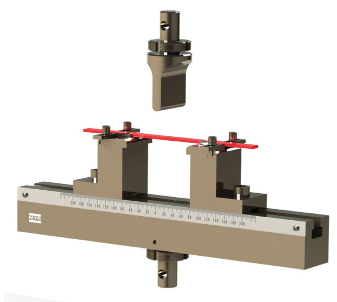


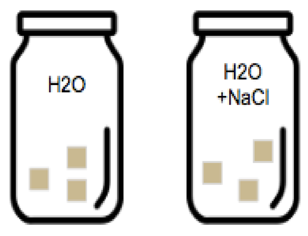
Electrical feed-throughs are surrounded by a hermetic glass seal that prevents water flow into the battery and circuitry of the device [3]. This glass seal is still susceptible to corrosion when it is exposed to ions found in blood and other physiological fluids.

As these devices are being miniaturized, the viscosity of the sealant must be lowered. To do so, manufacturers add toluene which acts as diluent in these epoxy systems. Medtronic engineers are unsure how this effects transport properties.

Experimental Procedure

3-Point Bend: HDP420 resin and hardener were combined at a 2:1 ratio and mixed with Toluene concentrations of either 0,10, and 20 wt.% Toluene. Six samples of each concentration were mixed and cured for either 25, 35, 45, 60, or 90 minutes to create 76x25x3mm bars later subjected to 3PB testing.



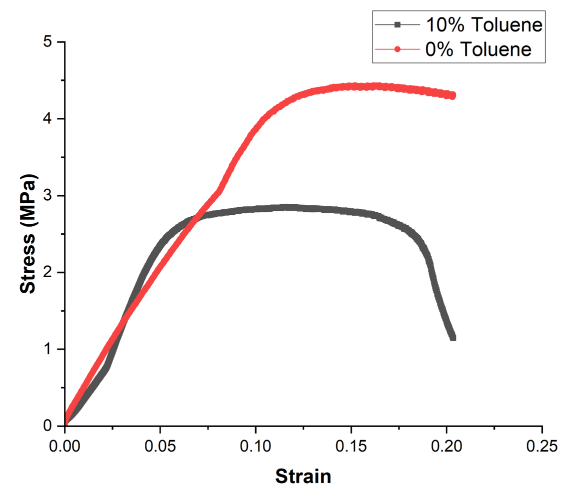


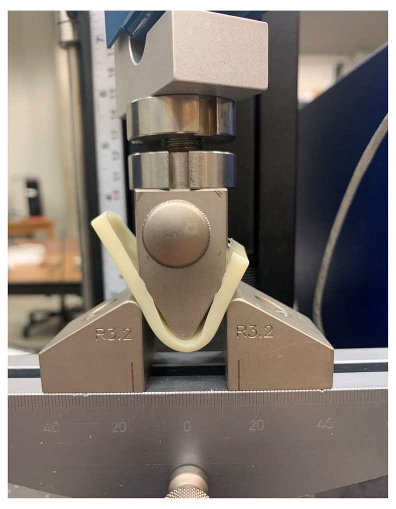
Absorption: HDP420 was mixed with concentrations of 0,10, 20, 30 wt.% toluene to create cubes of 1 cm^3 cured at 60ºC for 35 minutes. Each of the cubes was soaked in individual vials containing solutions of either just DI water, low salt, or high salt concentrations.

Differential Scanning Calorimetry (DSC): Samples of differing toluene concentrations used for 3PB were repurposed for DSC by removing ~15mg of each. These sections were loaded and run to a max temperature of 250ºC using a rate of 10ºC/minute. Additionally, beads of 20 wt.% solvent were run through the instrument to a temperature of 175ºC at a rate of 20ºC/minute to determine if annealing has any effect on sample properties.

Results & Discussion

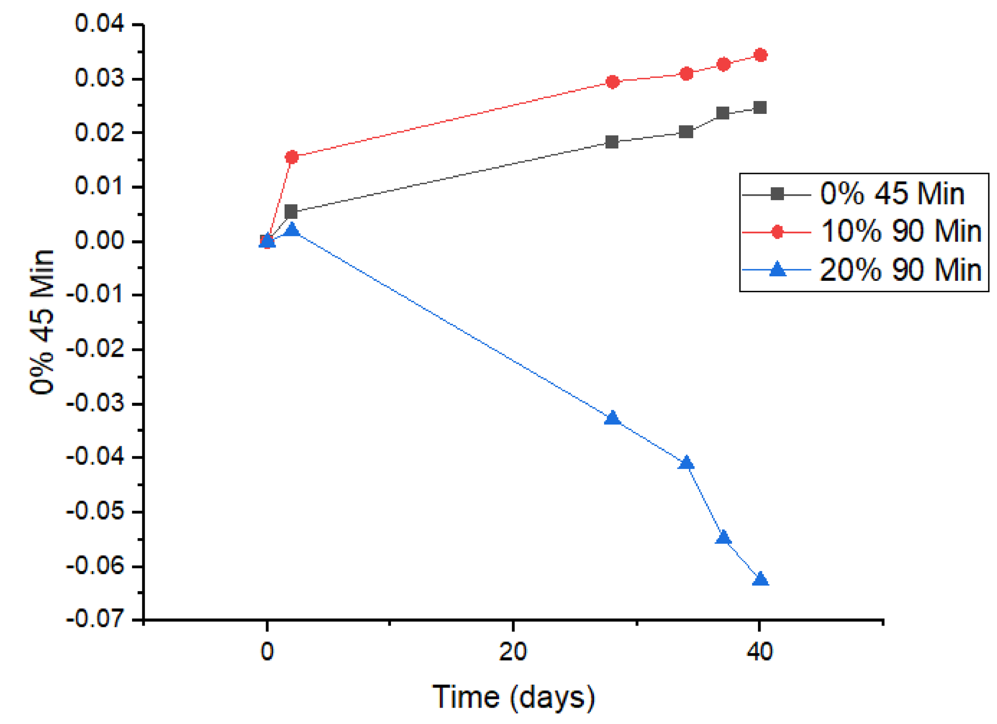
3-Point Bend: 3-point bend testing was performed to evaluate the curing properties of epoxy samples. Ideally, each sample would fail and show decreasing yield strength. However, 30 wt.% toluene samples were so ductile they never fractured, so a yield stress could not appropriately be determined. This behavior is shown in the image below. The 0 and 10 wt.% samples showed predictable behavior and through testing of samples at different curing times, an optimal cure time of 45 minutes for 0 wt.% toluene and a cure time of 90 minutes for 10 wt.% and 20 wt.% toluene was decided on as anything above these cure times did not yield significantly stronger samples.



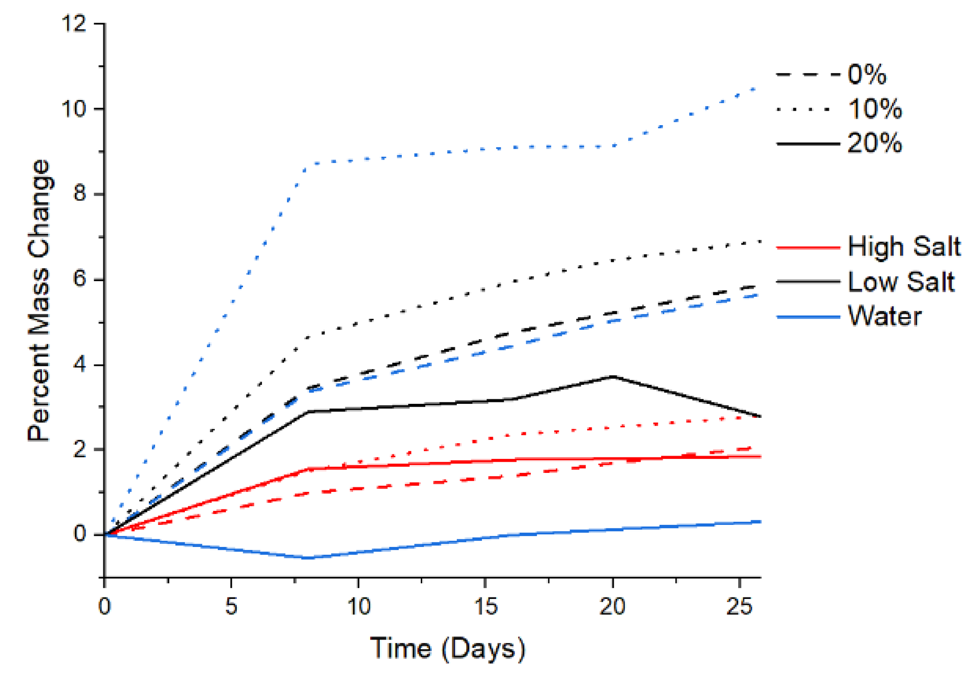


Results & Discussion

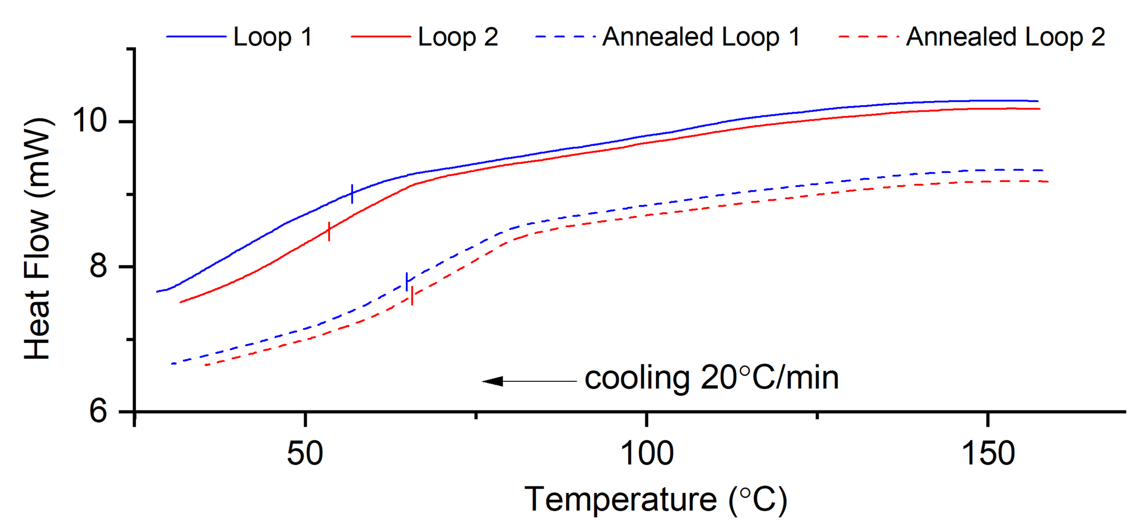
Swelling Tests: Swelling tests were done in order to observe the transport of water through the epoxy system. The hypothesis that the presence of toluene increases mesh size would lead to an increased mass transfer in higher epoxy samples, but this was not what was seen in these tests. High diluent samples showed a decrease in mass as shown below. 10wt.% toluene samples consistently increased in mass more than 0 wt.% toluene, however this difference was often very small. It is possible that water is replacing the toluene remaining in the system after curing. Although toluene is less dense than water, the polarity of water and the nonpolarity of toluene may be contributing to this mass loss.



Swelling in Hysol epoxy was also investigated, and the data for this test is shown below. Hysol exhibited almost identical trends to the DP420 epoxy used for all other experiments, but 20% samples lost mass less than other samples. The effect of salt concentration is also shown here. Low salt and water samples are often very similar, but high salt samples seem to swell very differently. Each high salt sample swelled very slightly and similarly.



Differential Scanning Calorimetry (DSC): DSC was performed to understand the effects of curing time on structural properties of the epoxy. To determine whether residual toluene was evaporating during the DSC process, samples were heated up to 175°C and cooled down to 25°C twice, and the loops were compared. One sample only had 90 minutes of curing time at 60°C, while the other had that same amount of curing with an additional 4-hour annealing treatment at 100°C.

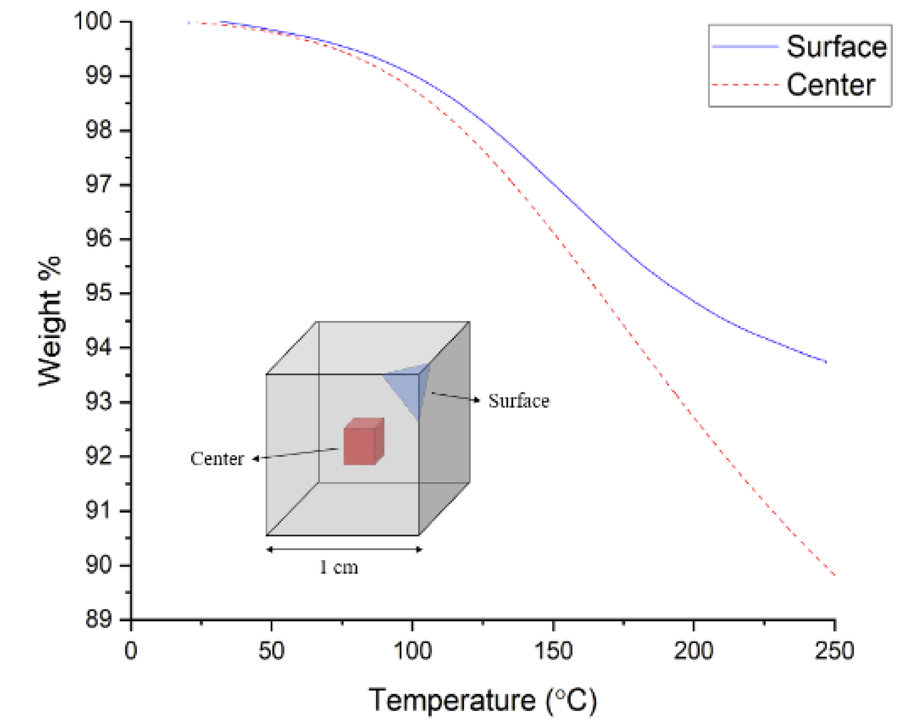


Effect of Annealing on Glass Transition Temperatures				
Sample	Loop 1	Loop 2	Annealed Loop 1	Annealed Loop 2
Tg (°C)	56.69	53.72	65.01	65.33

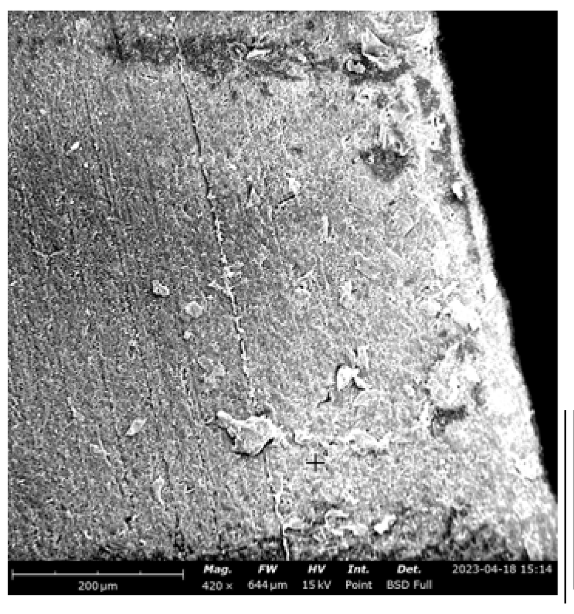
DSC data and resulting glass transition temperatures (Tg) are shown in the graph and table above. The unannealed samples showed a larger difference in Tg of approximately 3°C. The annealed sample maintained a more consistent Tg and showed an overall similar behavior between loops compared to the unannealed sample.

Results & Discussion

Thermogravimetric Analysis (TGA): TGA was performed to assess whether there was a greater concentration of toluene trapped in the center of the cube-shaped sample compared to the surface after 45 minutes of curing at 60°C. From the data shown below, it can be seen that the sample extracted from the center of the cube lost ~ 10 wt.% compared to the sample taken from the surface of the cube, which showed a loss of ~ 5 wt.%



Energy-dispersive X-ray Spectroscopy (EDS): EDS was done in an attempt to determine the level of salt transmitted through the network directly. High salt samples soaking for 70 days were used. Unfortunately, no salt was seen in the network. The presence of silicon was noticed, which should be in the polymer according to 3M.



30 wt.% salt was used in these soaks, so the salt concentration at the surface should be high enough to see in EDS but unfortunately none was observed. This EDS is from a 30 wt.% toluene sample which should be the easiest for salt to diffuse through.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	47.93	51.32
6	C	Carbon	45.72	36.75
14	Si	Silicon	6.35	11.93

Conclusions & Recommendations

One of the main conclusions of this study is that it is very difficult to remove solvents completely from polymer networks. This conclusion was confirmed by mechanical testing, DSC, and swelling tests. DSC revealed that annealing provides residual toluene more time and energy to evaporate out of the system and allows for more consistent structural properties like glass transition temperature. The swelling behavior of diluted epoxy samples is complicated and should be explored further. There also needs to be a larger emphasis on directly measuring ionic transport, although this proved to be a difficult task as no ionic salt was seen even in high salt samples which should have had a large mesh size.

Acknowledgments & References

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References

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