Spring 2023

Structural Design and Application of Polymeric Silicon Elastomers

Jacob Wyant
jw233@uakron.edu

Recommended Citation

Wyant, Jacob, "Structural Design and Application of Polymeric Silicon Elastomers" (2023). *Williams Honors College, Honors Research Projects*. 1714.
https://ideaexchange.uakron.edu/honors_research_projects/1714

Executive Summary

The purpose of this project was to determine how the polymeric structure and mechanical properties of the polydimethylsiloxane elastomer are affected by the ratio between the polydimethylsiloxane (PDMS) macromolecular chains and the crosslinkers (vinyl-PDMS). These were determined via tensile and compression testing. Then, application testing was performed, which involved the addition of spiropyran (SP) to observe how this fluorescence and crosslinking agent affected the elastomer (SP-PDMS).

From the mechanical properties testing, the elastomers with a higher ratio of crosslinker to macromolecular chain could withstand higher tensile and compressive strains but failed at lower stresses than their counterparts with lower concentrations of crosslinkers. The elastomers were also found to have significantly less surface interactions with water than the hydrogel. This is exhibited by the increased sphericity of the water droplets on elastomer samples and by the significantly longer time required to melt ice crystals when compared to the same droplets on hydrogels.

Major recommendations include more testing of the elastomer's icephobic properties, such as using an infrared (IR) camera to observe the flow of heat between the elastomer/hydrogel sample and the water droplet and repeating the slide angle tests with a machine instead of by hand.

Regarding possible applications of SP-PDMS elastomer, its ability to continuously absorb UV rays and maintain its transparency means it could be used in transition sunglasses or as a windshield coating to protect users from harmful radiation. Its hydrophobic properties further lend it to the application as a windshield coating as the elastomer coating would mitigate ice accumulation in winter months and any accumulation would be easier to remove. When its fluorescence is activated by strain on the elastomer, it could also serve as an indicator of the strain a system is under, such as an early warning indicator on structural supports.

Personally, I gained hands-on experience doing tests I previously had only read about. Running tensile and compression tests was new to me, as previously I had only learned about them in class. I also learned a great

deal about elastomers, by nature of the project focusing on them. The project also caused me to reevaluate how I thought about crosslinkers and how they could affect mechanical properties. I initially assumed that higher amounts of crosslinkers would result in a stronger elastomer, but the reverse occurred. Thus, this project required that I think critically and challenge my assumptions.

Table of Contents

Introduction

The scope of this investigation was to determine how the ratio of polymeric structure and mechanical properties of the PDMS elastomer are affected by the ratio between the polydimethylsiloxane (PDMS) macromolecular chains and the crosslinkers (vinyl-PDMS and spiropyran). These mechanical properties were determined via tensile and compression tests. Then, we inspected how the addition of a fluorescence agent, spiropyran (SP), affected the properties of the elastomer and performed application testing with regards to the fluorescent and icephobic properties of the elastomer.

Background

PDMS can be crosslinked via two different methods, either through the use of UV radiation to generate free radicals that initiate the crosslinking or via a platinum catalyst. The radiation method is more difficult to mediate and requires more extreme conditions, so catalyst-assisted crosslinking was chosen for this investigation, further detailed in the Experimental Procedures section. This reaction is shown below in Figure 1.

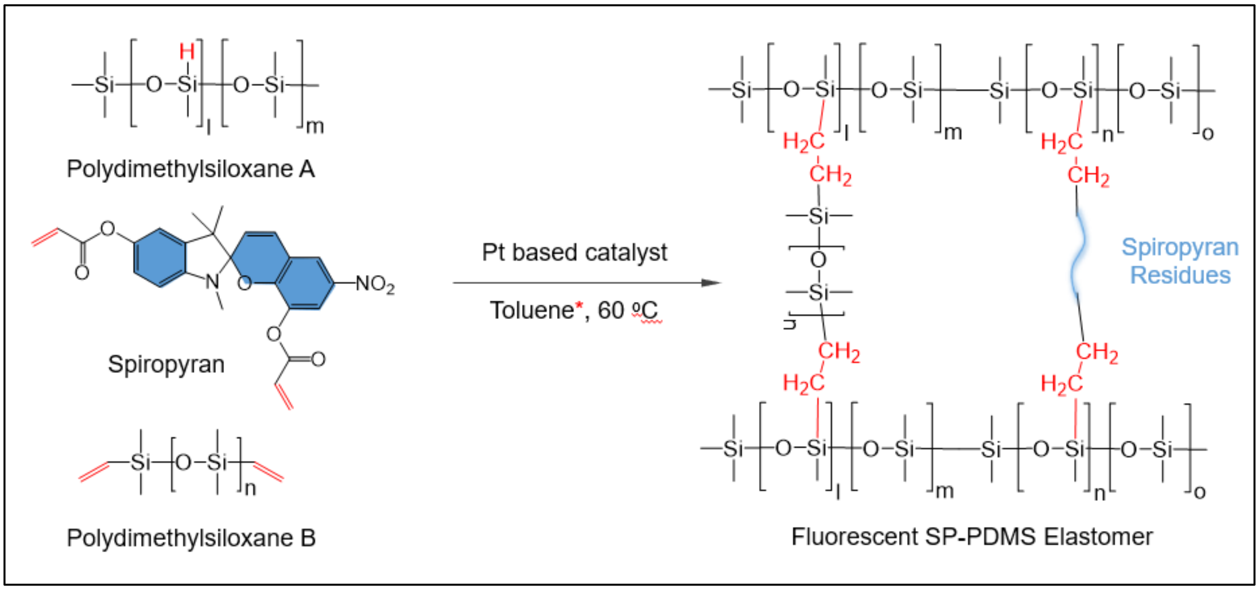


Figure 1 – Shows the crosslinking reaction. Sylgard A consists of macromolecular chains, linked via either spiropyran or Sylgard B at the bonds highlighted in red.

A secondary crosslinker, spiropyran (SP), was introduced due to its ring-opening reaction when exposed to UV light to form merocyanine (MC), shown in Figure 2. This reaction produces a color change in the material and can also be initiated by application of force or heat, as demonstrated by Chen et al., 2017. The reverse reaction (MC→SP) occurs when exposed to white light, allowing the SP-PDMS to continually absorb UV light in outdoor environments. The addition of SP turns PDMS into a stimuli-responsive elastomer, capable of responding to environmental cues. The addition of SP should also allow the elastomer to recover from deformation via the MC→SP reaction as demonstrated by Chen et al. with hydrogels containing SP.

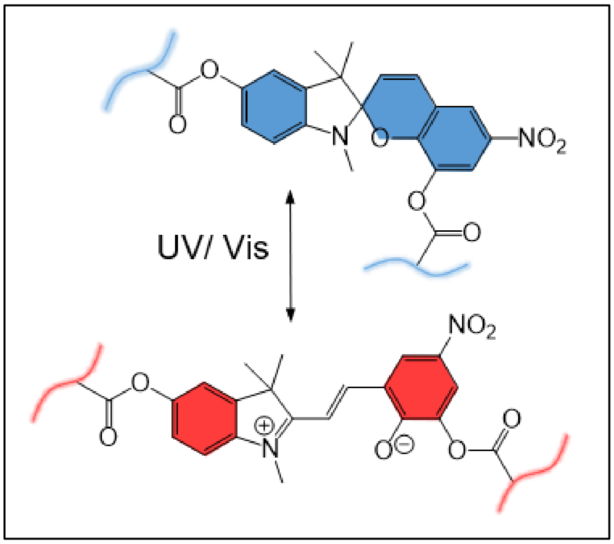


Figure 2 – Shows the structural change of spiropyran (blue) to merocyanine (red) caused by exposure to UV radiation. This is also known as a photochromatic reaction due to the change in color of the material caused by exposure to light.

Icing is a consistent problem for large swathes of the world, costing time and money every year. Thus, it is desirable to find ways to mitigate the accumulation of ice on surfaces. PDMS has been used as an icephobic coating due to its hydrophobic nature, which prevents droplet accretion and therefore ice nucleation. This is what Zhang et al. refer to as a dry antifreezing material due to the lack of water in its makeup.

Experimental Procedures

Elastomer Synthesis

The elastomer used in this investigation consisted of the Sylgard 184 Silicone Elastomer Base and Silicone Elastomer Curing Agent, respectively referred to as Sylgard A and B. To determine how the mechanical properties of the elastomer were affected by the ratio of PDMS chains to crosslinker, multiple samples were synthesized at the following mass ratios of Sylgard A to Sylgard B: 10:1, 12:1, 16:1, and 20:1. The compounds were massed out and mixed well, then either poured into a Petri dish or a syringe and allowed to degas. The different geometries allowed separate tests to be run on the same mixture, the flat disc was cut to provide samples for the tension testing and the cylindrical sample was used for the compression testing. After degassing, the samples were placed in an oven at 60°C overnight to cure.

When synthesizing fluorescent SP-PDMS, the only change is that a small amount of spiropyran (SP), approximately a one-thousandth of the solution’s mass, was dissolved in toluene and mixed into the elastomer sample before degassing.

Hydrogel Synthesis

The hydrogels used were synthesized according to the procedures in Zhang et al., 2021.

Determination of Mechanical Properties

The samples’ mechanical properties were tested via a universal tensile machine (Instron 3345, MA) with a 500 N transducer at the stretching rate of 100 mm/mm. Here, the tensile strain (ε) will be defined as the extension distance ($\triangle L$) divided by the initial length (L_0). This test will allow us to measure their tensile and compressible properties. The as-prepared elastomers are cut into a dumb-bell shape with a width of 3.18 mm, a gauge length of 25 mm, and an approximate thickness of 1.0 mm for these tests.

UV-Vis and Optical Behavior

To compare how SP-PDMS responds to whole spectrum light vs. only UV light, various experiments were carried out:

Outdoor Experiment

The sample was taken outdoors on a sunny day, where it was first held and stretched in a shady area, then held under sunlight for approximately 30 seconds, during which the color change was observed. To prove that there was no loss of mechanical properties, the fluorescing elastomer was then stretched again. The test was filmed using an iPhone camera and stills taken from the video, see Figure 3.

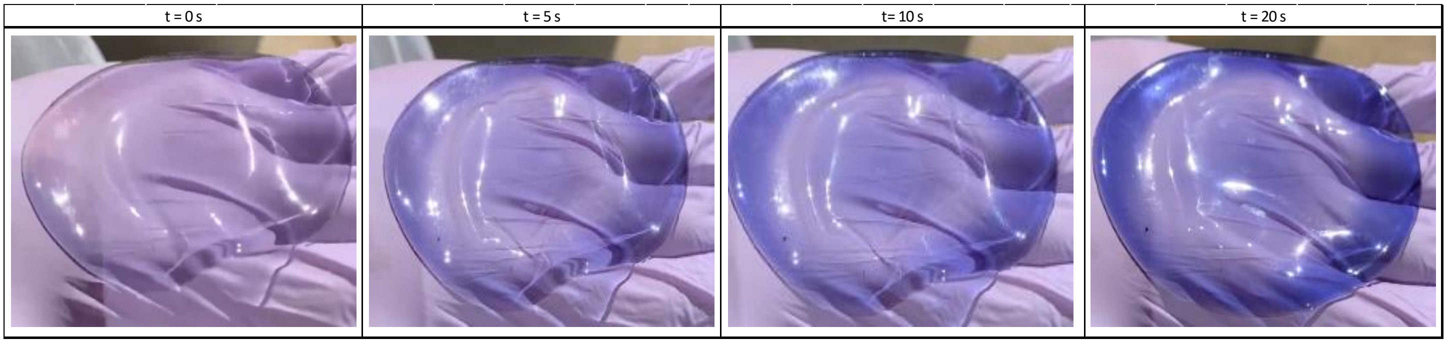

t = 0 s | t = 5 s | t= 10 s | t = 20 s

Figure 3 – Shows the progressive photochromic reaction of SP→MC in sunlight. Banded nature is due to how the material set in the Petri dish it was cured in.

Indoor Experiments

A SP-PDMS sample was placed under a UV light in a dark room. The UV light was then turned on to observe how the SP-PDMS fluoresced under these conditions and a picture taken every 6 seconds for a minute, see Figure 4.

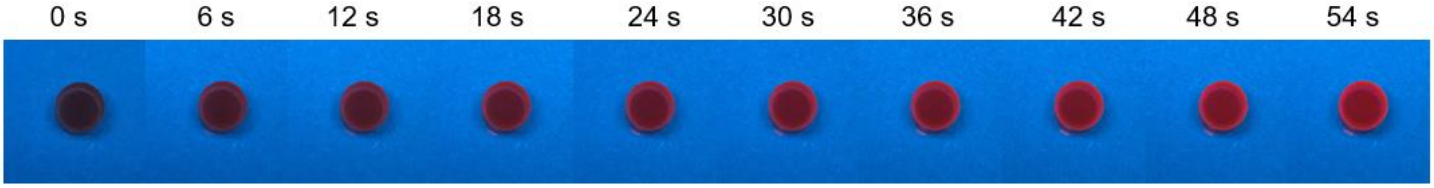


Figure 4 – Shows how SP-PDMS responds to only UV light in a dark room.

A second experiment was conducted where a UV light was passed over the sample at a constant rate, resulting in different exposure times on each run. The intensity and wavelength of the emitted light were recorded and graphed, shown in Figure 7.

Icephobic Property Testing

Sliding Angle Testing

Different surfaces were positioned on a machine at 0˚ and a drop of water (10 μL) placed on the surface. The water droplet's shape and behavior were recorded (sphericity, did the droplet spread out, etc). The surface was tilted and the angle at which the water slid from the surface was recorded. Due to issues controlling the slide plate angle due to moving it by hand, this data was imprecise and not included in the report.

Surface Interaction Testing

Water droplets (10 μL) were placed on samples of elastomer or hydrogel and placed in a freezer until the droplet was completely frozen. They were then removed from the freezer and placed under a microscope to observe the melting of the ice crystal. Pictures of the melting ice crystal were taken intermittently using an iPad hooked up to the microscope.

Data & Results

Mechanical Properties

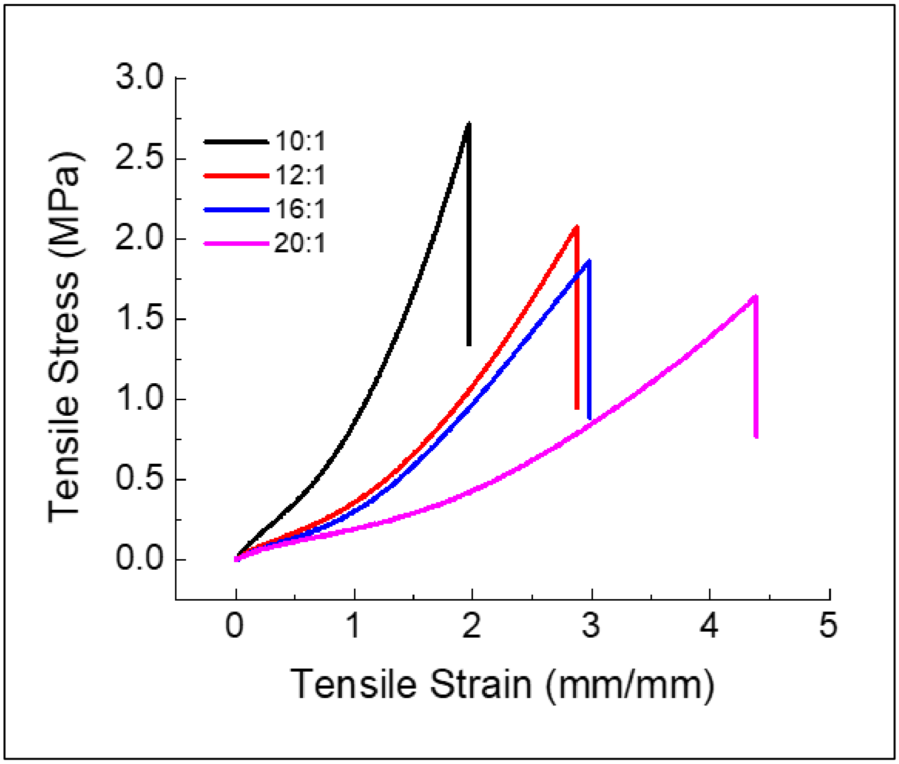


Figure 5 – Graph that shows how the tensile properties of the PDMS elastomer are affected by the ratio of macromolecular chains to crosslinking agents, aka Sylgard A to Sylgard B.

Table 1 – This table details some of the highlights from Figure 5, such as maximums for load, tensile strain, and tensile stress as well as the Young's modulus for each sample.

Ratio (A:B) (X:1)	Load at Max Tensile Strength (N)	Max Tensile Stress (MPa)	Tensile Strain Max (mm/mm)	Young's modulus (10-40%) (Mpa)
10	8.63	2.72	1.97	0.692
12	6.58	2.07	2.87	0.364
16	5.91	1.86	2.98	0.304
20	5.21	1.64	4.38	0.280

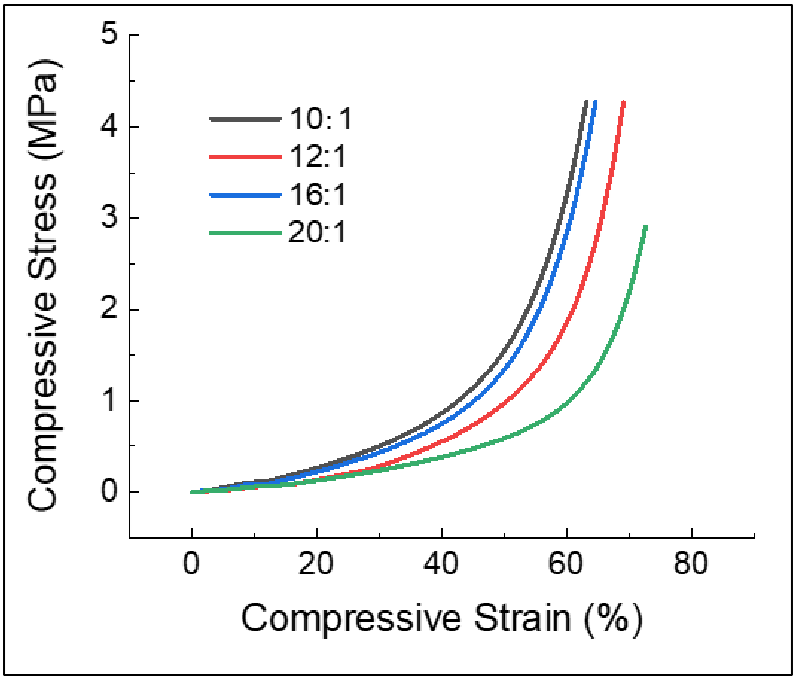


Figure 6 – Shows how the compressive properties of the elastomer were affected by the ratio of Sylgard A to Sylgard B.

From the testing of the mechanical properties, there was a direct correlation between the ratio of PDMS chains to crosslinker and the tensile properties of the elastomer. Samples with a higher ratio of crosslinker to chains could withstand a greater elongation before breaking but broke at lower stresses than elastomers with lower ratios of crosslinkers. This is similar to results from Katz et al., which was attributed to the formation of aggregates in the PDMS matrix reducing the elastomer's ability to disperse stress.

UV-Vis Behavior

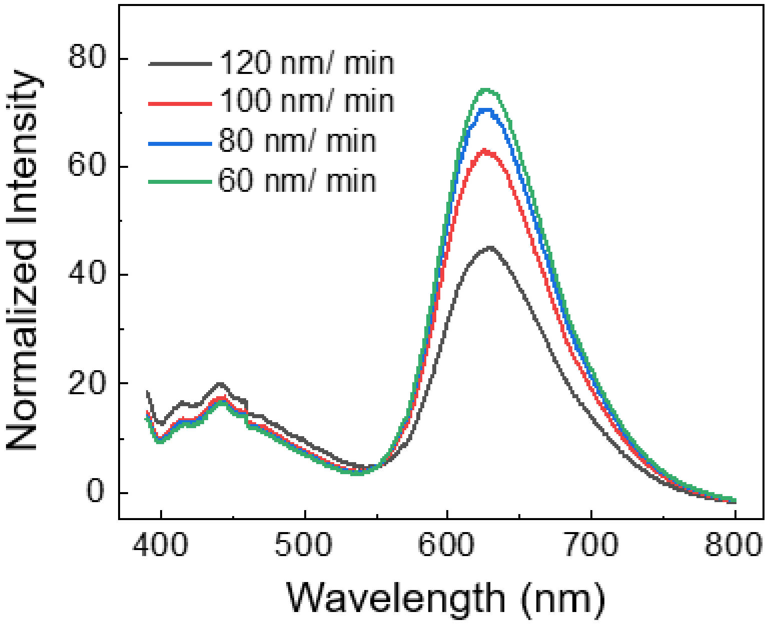
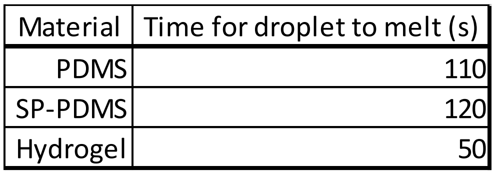


Figure 7 – Graph of intensity of the emitted light vs the wavelength of the emitted light. The light was passed over the sample at different rates, as shown by the legend, which resulted in different exposure times.

Figure 7 shows an increase in the intensity of the fluorescence given off by the SP-PDMS as the exposure time increases, an effect also seen in Figure 4. The peak of these graphs is in the 600-650 nm range, which explains the red fluorescence shown in Figure 7. Shown by the variation in fluorescence in Figure 3, the concentration of SP also has a major effect on the elastomer's ability to absorb UV light and fluorescence. This allows designers to control the elastomer's fluorescent properties based on the application they intend to use it for.

Surface Interactions

Table 2 – The results of the surface interaction testing, shows how long the droplet of water took to melt on each sample.



Material	Time for droplet to melt (s)
PDMS	110
SP-PDMS	120
Hydrogel	50

On a hydrophobic sample, the water droplet retains a more spherical shape which decreases the amount of surface area contacting the droplet and in turn decreases the heat flow from the sample into the droplet. Therefore, a longer time to melt indicates that there is less surface interaction between the sample and the droplet and that the sample is more hydrophobic. As seen in Table 2, both elastomers are, unsurprisingly, significantly more hydrophobic than the hydrogel. There is not a significant difference between the PDMS and SP-PDMS, likely due to the relatively low amounts SP used in the elastomer.

Conclusions & Recommendations

The hydrophobic and photochromic nature of SP-PDMS lends it to applications such as window or windshield coatings, where the UV absorption protects users from harmful radiation while also preventing an accumulation of ice on these surfaces during winter months. Similarly, the photochromic reaction means that the elastomer could also be utilized as a coating to create transition sunglass lenses or similar products. Finally, SP-PDMS can function as a sensor for heat, light, or stress in a variety of applications.

Recommendations for future research include more testing of the elastomer’s icephobic properties, such as using an infrared (IR) camera to observe the flow of heat between the elastomer/hydrogel sample and the water droplet as well as repeating the slide angle tests with a machine instead of by hand. The ability of SP crosslinks to recover mechanical properties, as demonstrated by Chen et al. (2017, also merits more research. They proved it worked remarkably well for a SP-linked hydrogel, so it should also be possible for an SP-linked elastomer.

References

Chen, H., Yang, F., Chen, Q., & Zheng, J. (2017). A Novel Design of Multi-Mechanoresponsive and Mechanically Strong Hydrogels. *Advanced Materials*, *29*. doi:10.1002/adma.201606900

Katz, S., Lachman, N., Hafif, N., Rosh, L., Pevzner, A., Lybman, A., . . . Rotter, H. (2023). Studying the Physical and Chemical Properties of Polydimethylsiloxane Matrix Reinforced by Nanostructured TiO2 Supported on Mesoporous Silica. *Polymers*, *15*(1), 81. doi:https://doi.org/10.3390/polym15010081

Zhang, D., Liu, Y., Liu, Y., Peng, Y., Tang, Y., Xiong, L., . . . Zheng, J. (2021). A General Crosslinker Strategy to Realize Intrinsic Frozen Resistance of Hydrogels. *Advanced Materials*, *33*. doi:10.1002/adma.202104006