LA-UR-17-28093
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Intended for: Report

Issued: 2017-09-08

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Crosslinking of SAVY-4000 O-rings as a Function of Aging Conditions

UO Summer 2017

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Abstract

SAVY-4000 containers were developed as a part of DOE M 441.1-1 to protect workers who handle stored nuclear material from exposure due to loss of containment.[1] The SAVY-4000 is comprised of three parts: a lid, a container, and a cross-linked fluoropolymer O-ring. Degradation of the O-ring during use could limit the lifetime of the SAVY-4000. In order to quantify the chemical changes of the O-ring over time, the molecular weight between crosslinks was determined as a function of aging conditions using a swelling technique. Because the O-ring is a cross-linked polymer, it will absorb solvent into its matrix without dissolving. The relative amount of solvent uptake can be related to the degree of crosslinking using an equation developed by Paul Flory and John Rehner Jr[3]. This method was used to analyze O-ring samples aged under thermal and ionizing-radiation conditions. It was found that at the harsher thermal gaining conditions in absence of ionizing-radiation the average molecular weight between crosslinks decreased, indicating a rise in crosslinks, which may be attributable to advanced aging with no ionizing radiation present. Inversely, in the presence of ionizing radiation it was found that material has a higher level of cross-linking with age. This information could be used to help predict the lifetime of the O-rings in SAVY-4000 containers under service conditions.

Introduction

The Department of Energy (DOE) M 441.1-1 was issued to protect workers who handle nuclear material from loss of containment of stored materials. As a part of this mandate, the SAVY-4000 (named for the four designers, Stone, Anderson, Veirs, and Yarbro) was developed to safely store actinides outside of an approved engineered-contamination barrier[2]. The SAVY-4000 is a stainless steel container made up of three main components, the lid, the container, and the fluoropolymer O-ring compressed radially between the two to create a seal (figure 1). The O-ring has been determined to be one of the life-time limiting factors of the container due to it being vulnerable to elevated temperature, compression, and ionizing-radiation. As a part of the DOE manual's requirement to maintain and survey the containers to establish confidence that are in working condition, the O-ring is replaced once every five years. Due to the high costs of handling the stored nuclear material combined with the large number of containers that are projected for future use it results in huge costs to stay in compliance with the current DOE M 441.1-1 timeline. Therefore MST-7 is a part of a multi-group effort to extend the life-time of the container by characterizing the degradation mechanisms of the O-ring and confidently predicting an accurate lifetime that is up to 9 times longer than the current. Ideally this would reduce the overhead cost to storage and adhere to As Low As Reasonably Achieving (ALARA) guidelines to radiation exposure for workers.

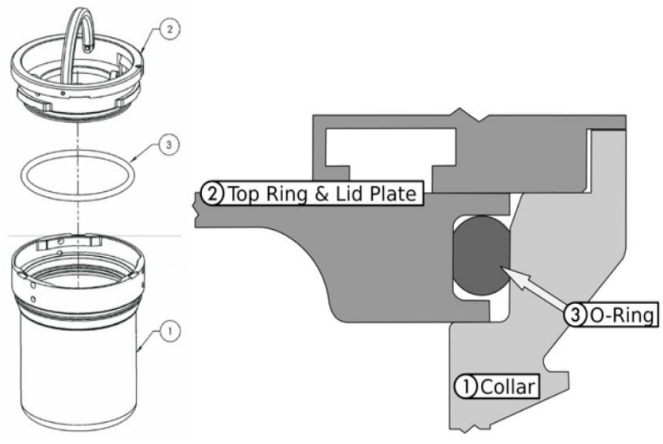
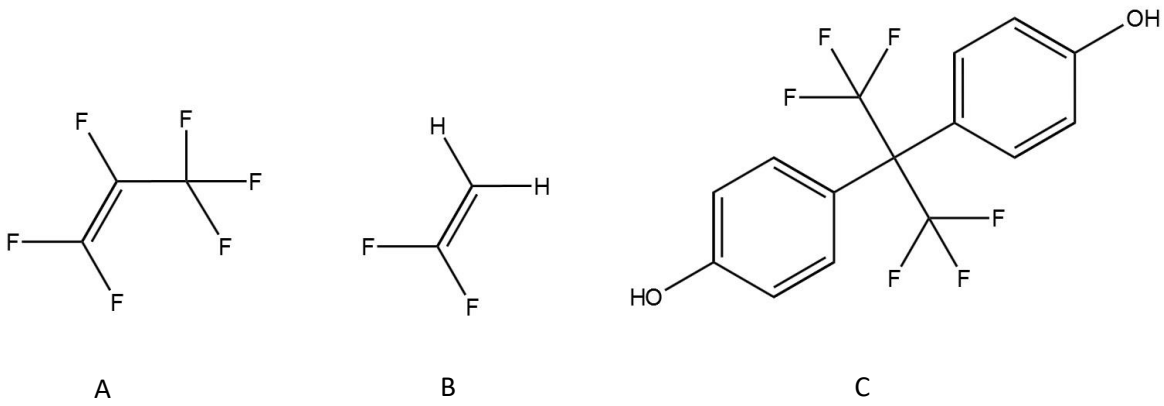


Figure 1: (Left) The SAVY-4000 containers three parts, the container (1), the lid (2), and the O-ring (3). (Right) The cross-section of the SAVY-4000 container showing the O-ring (3) compressed between the lid (2) and container (1). Image from Weiss *et al.* (2016)

Currently not much is known about the degradation of the cross-linked hexaflouropropylene and vinylidene fluoride co-polymer O-ring (figure 2). Previous research suggests that it is a robust material, rarely showing failure even at extreme thermal aging conditions[2].



A B C

Figure 2: The O-ring is commercially available from Parker and is a copolymer of A) hexaflouropropylene monomer and B) vinylidene fluoride. It is cross-linked with C) bisphenol-AF (CITE).

In order to further elucidate the degradation mechanism of this material, the crosslinking as a function of accelerated aging was determined for samples exposed to thermal and ionizing-radiation conditions.

Aging

All samples were placed between bolted steel plates that were set at 4.0 ± 0.03 mm with spacers to recreate their working compression. A large set of samples was thermally aged by placing them in ovens set at a designated temperature (70 – 210 °C) for the designated amount of time (up to 30,000 hours); a sub-set of these thermally aged samples (described in Table 1a) was subjected to the swelling experiments herein. Another set of samples was also aged under thermal and ionizing radiation according to table 1b. This set was aged at the Gamma Irradiation Facility (GIF) at Sandia National Laboratory. For each experiment there were four ovens set at one temperature but each receiving a different total dose. Each experiment was run for a 72 hour period. Please note that for the 70 °C experiment the ovens tripped the breaker at some point during the experiment, so this temperature is actually a gradient from 70 °C to room temperature over a 72 hour period.

Table 1a (top) and 1b (bottom): The aging conditions for fluoropolymer O-ring samples.

Temperature (°C)	
70	0
70	20
70	50
70	100
70	5000
70	5800
90	0
90	5
90	10
90	50
90	14000
120	2154
120	5000
160	50
160	3162
160	13656
160	23000
175	3162
190	147
190	912
210	1000

Temperature (°C)	Dose Rate (Rad/s)	Total Dose (Mrad)	Time (Hours)
RT	4.32	1.120	72
RT	4.32	1.234	72
RT	4.32	1.555	72
RT	4.32	2.576	72
70-RT	4.73	1.120	72
70-RT	4.73	1.234	72
70-RT	4.73	1.555	72
70-RT	4.73	2.576	72
160	6	1.120	72
160	6	1.234	72
160	6	1.555	72
160	6	2.576	72
210	9.94	1.120	72
210	9.94	1.234	72
210	9.94	1.555	72
210	9.94	2.576	72

Molecular Weight between Crosslinks

Molecular weight between crosslinks was derived from swelling cross-linked materials and relating the amount of solvent uptake to the relative amount of crosslinks. The swelling was accomplished by placing approximately 1g O-ring samples in scintillation vials and immersing with Tetrahydrofuran (THF) and weighing after about 140 hours in solvent. This time point was determined to be the point at which the polymer reaches equilibrium with solvent. From this the volume fraction is calculated using equations 1 and 2.

$$\text{Volume at Equil. (mL)} = \frac{Final\ Weight\ (g)}{Density\ of\ Polymer\ (\frac{g}{mL})} + \frac{Final\ weight - Initial\ Weight}{THF\ Density\ (\frac{g}{mL})} \quad (1)$$

$$\text{Volume Fraction of polymer swollen} = \frac{Initial\ Volume\ of\ Sample}{Volume\ at\ Equil. * Density\ of\ polymer\ system} \quad (2)$$

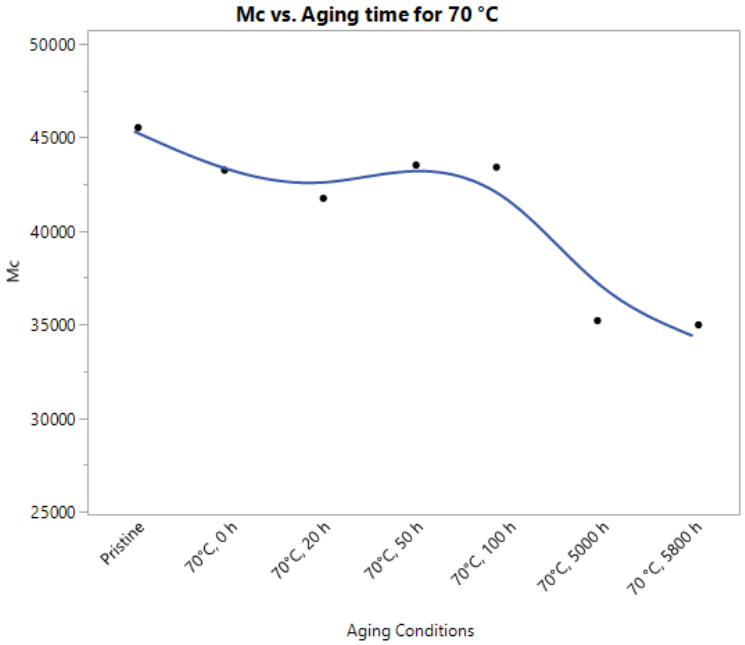
This characteristic of swelling without dissolving is due to the networked structures of cross-linked polymers. If a material has more crosslinks then its network structure will be tighter and it will expand less, taking up less solvent. The opposite is true for materials with less crosslinks because the network structures are looser. This theory was developed by Paul Flory and John Rehner[3]. Equation 1 was derived to quantify this in terms of molecular weight between crosslinks (M_c). This equation calculates M_c as a function of volume fraction of polymer swollen (υ, see equation 2), taking into account the density of the polymer system (ρ, where the flouropolymer O-ring has a density of about 1.86 g/mL), the molality of the solvent system used to swell (V_1, THF has a molality of 79.76 mL/mol), and the polymer solvent interaction parameter (K, 0.5 is used in this case[4]) as constants. K quantifies the chemical interactions between the polymer system and the solvent where a higher value indicates a greater chemical attraction and results in more swelling. Because this polymer/solvent system isn't as widely known as something like polyethylene, for example, the K being used in this study was assumed to be 0.5 based on an interaction parameter determined for a similar cross-linked fluoropolymer/THF system[4].

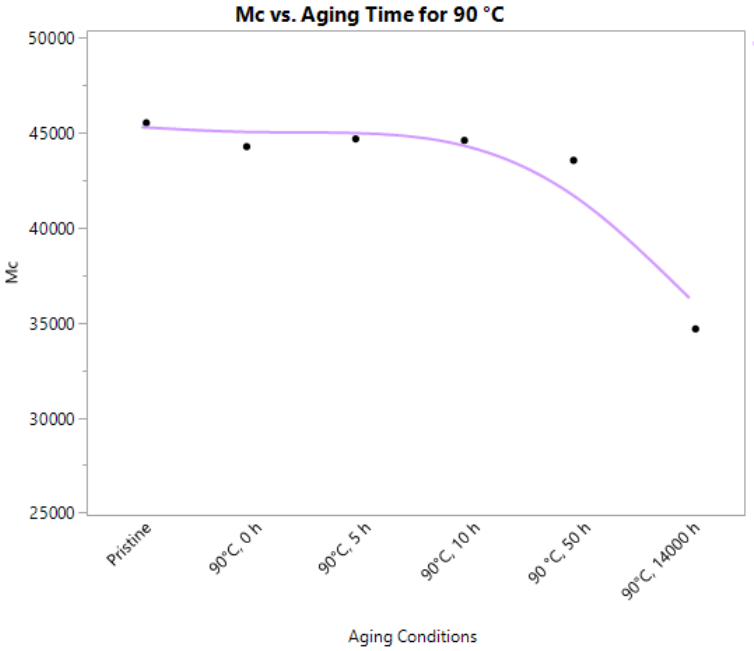
$$M_c = \frac{-\rho * V_1 * \upsilon^{1/3}}{K * \frac{\upsilon^2}{2} + Ln(1-\upsilon) + \upsilon} \quad (3)$$

Results/Discussion

Thermally Aged samples

The M_c for thermally aged samples was determined as well as the M_c for the pristine material for reference. Figure 2a-c shows the M_c M_c for the samples described in Table 1a; the results are shown in 3 plots that are organized according of aging condition. A smoothed line was added to each figure to indicate a trend in the M_c as the aging conditions become harsher. Within each set there is a trend of decreasing M_c with harsher aging conditions, indicating the material is becoming, on average, more cross-linked. In polymer systems elevated temperature mimics how the polymer system may act over long periods of time, thus it is likely that the trend at elevated temperatures may be indicating the dominant degradation mechanism for the O-ring over time is cross-linking. However, the sample that was aged at 210 °C for 1000 hours is a large outlier in the extreme aging conditions, the with M_c being near 135% the size of the pristine material. This indicated that at this aging condition chain scission was the dominant degradation mechanism.





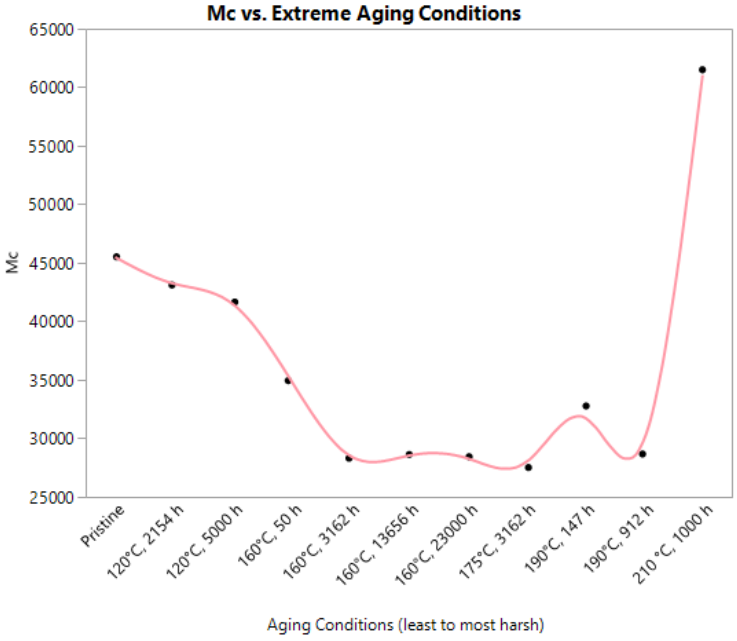


Figure 2a-c: a (top left) is the M_c vs. aging time for the samples aged at 70 °C, b (top right) is the M_c vs. aging condition for 90 °C, and c (bottom left) is the M_c for the most harsh aging conditions. 4c is organized so that each temperature is lumped together the ascending in aging time for that temperature. The line represented in each is a smoothed line meant to show trend in M_c.

The outlier at 210 °C could indicate that the material over an extremely long time could beginning to degrade via chain scission. It could also suggest that at this aging time and temperature a new degradation mechanism that is causing chain scission to be the dominant mechanism. It is likely that at any aging conditons both mechanisms are present, but that one takes dominance over the other. In the case of thermal aging, the crosslinking mechanism is dominant for most aging conditions and likely is the mechansism that realistically represents how the material behaves as it ages. 1000 hours at 210 °C may have been to harsh of an condition and caused the material to behave in a way that is not relevant to how it may act at room temperature over time. It could be useful to have more time points for 210 °C so that we can understand when exactly the material starts to degrade at this temperature.

Thermal and Radiation Synergistic Aging

This study was also looking at the synergistic effects of temperature and dose-rate on the M_c of the O-ring. The effect of dose rate and temperature on the M_c can be seen in figure 3a,b. At room temperature M_c decreases with increasing dose-rate indicating that increasing ionizing radiation results in higher relative crosslinking. This trend is also observed at 70 °C; however now that the material is undergoing two stresses the average M_c is higher indicating that temperature is causing the material to become less relatively cross-linked (as shown by a one-way anova and a student's t-test at the 95% confidence level in appendix). Though there is an observed difference in the data, because of the oven failure definitive statements cannot be made. But there is a large difference between the ambient temperature data at the that at 160 and 210 °C, supporting that higher temperature will likely result in a higher relative M_c (indicated by one-way anova and student's t-test in appendix). But there is a lot of noise in these data points likely because at the temperature and radiation (210 °C, which was an outlier in the thermal analysis as well, and 9.94 rad/s = 2.5 million rad over a 72 hour period, where only 1000 rad is fatal to humans[5]) is so harsh that there could be multiple degradation mechanisms competing for dominance. Looking at the general trends, temperature (which can be indication of time) in the presence of ionizing-radiation causes the material to undergo chain scission (higher M_c), but increasing levels of ionizing-radiation cause the material to crosslink more. Predicting the behavior of this material over its life-time, it is likely that in the presence of ionizing-radiation (at least at the levels of 4.32 rad/s and higher) the material degrades dominantly by chain scission as it ages under ionizing radiation, but as radiation increases there will be further crosslinking. Even though with increased temperature there is relatively lower cross-linking all of the synergistic M_c's are below the pristine M_c indicating that though both mechanisms are competing, there is still an overall preference towards cross-linking.

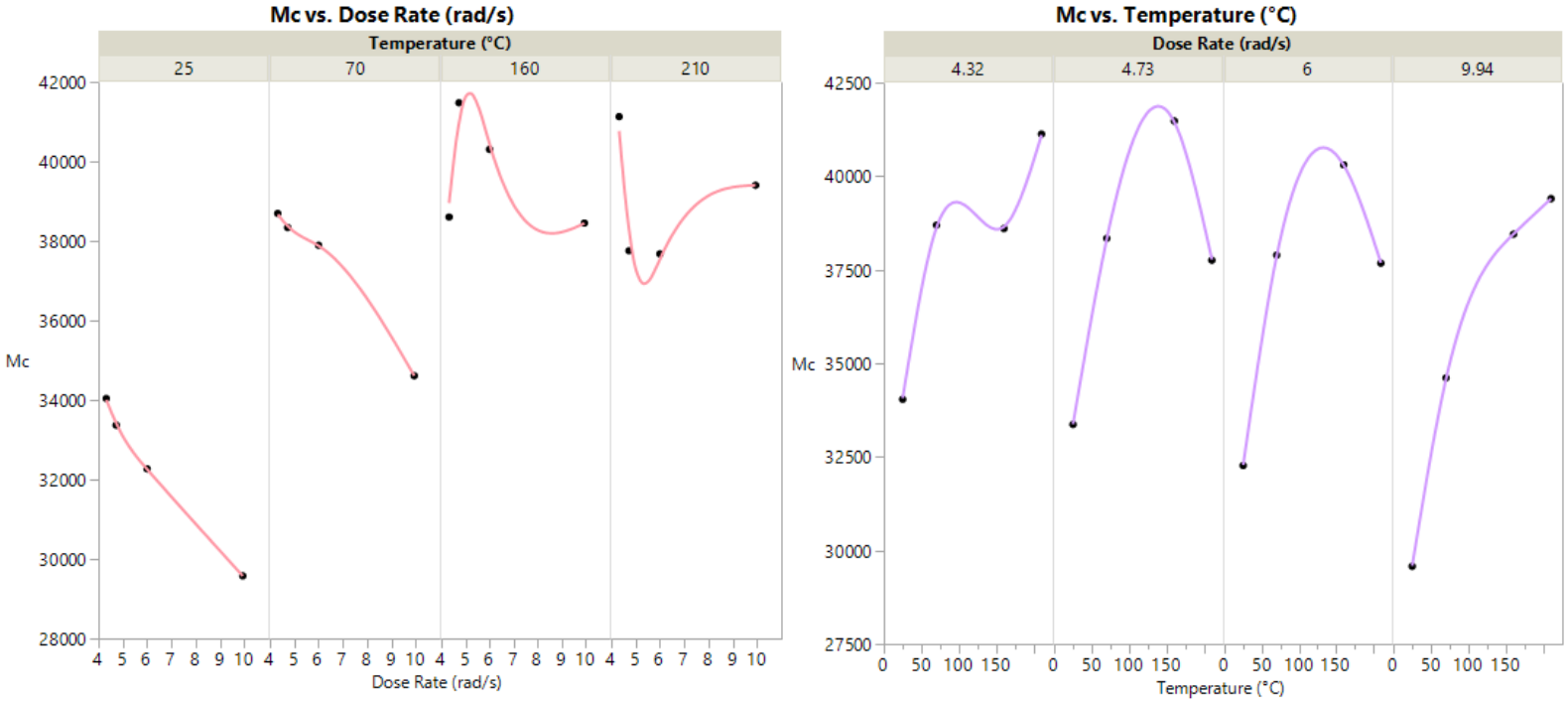


Figure 3a,b: a (left) the M_c as a function of dose rate for each temperature block. b (right) the M_c as a function of temperature for each dose rate.

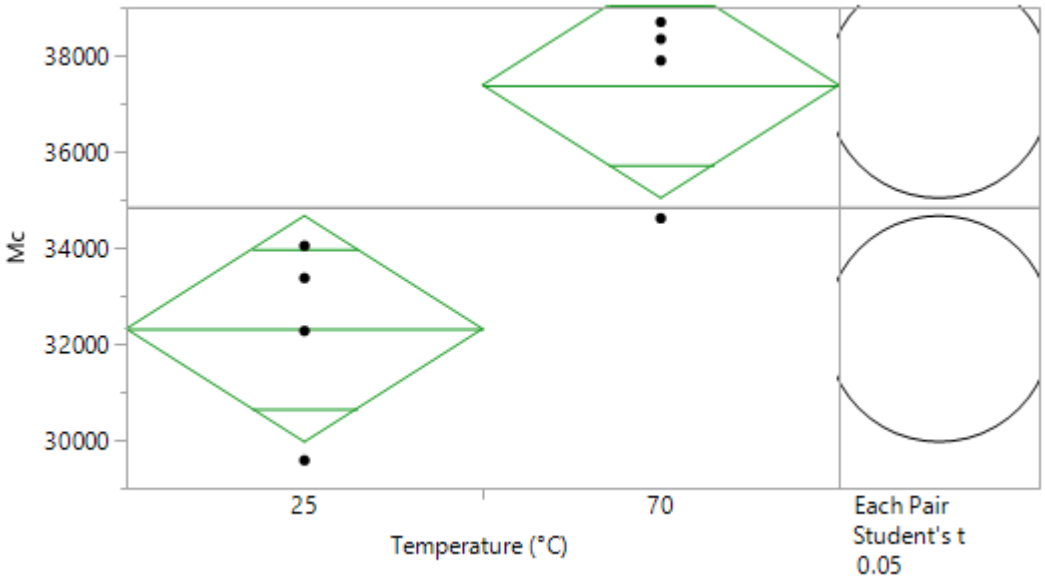
Conclusion

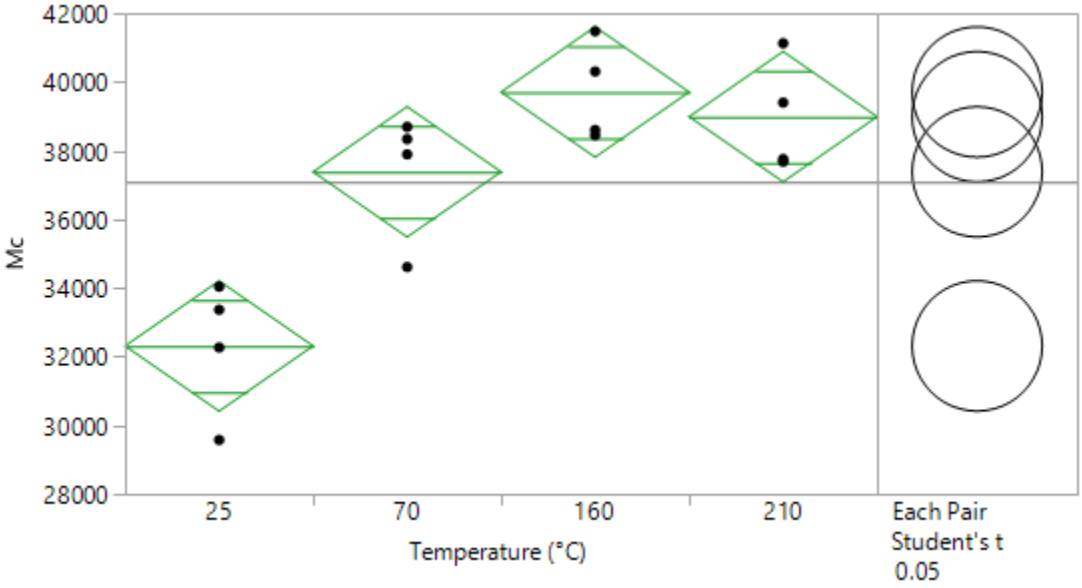
As a part of DOE M 441.1-1 and accurate life-time prediction for the storage containers of actinides must be made in order to protect workers from loss of containment. The flouropolymer O-ring is the lifetime-limiting part of the SAVY-4000 containers and it is currently replaced every five years resulting in a huge cost for the laboratory to maintain compliance. Previous research suggests that the life-time of these containers is much longer than 5 years, therefore the degradation mechanism overtime was determined to provide more insight into the prediction of life-time for the O-rings. Under no ionizing-radiation conditions the primary degradation mechanism was determined to be further relative cross-linking using a solvent swelling technique. Under ionizing radiation conditions, it is likely that the primary mechanism may be a mix of crosslinking and chain scission with further cross-linking being the dominant mechanism. Understanding these degradation mechanisms will provide information to make an accurate life-time prediction of the O-ring that will result in saving money storing these materials while also keeping workers who handle the storage of these materials safe.

Acknowledgements

I would like to acknowledge Matthew Herman, Alumni of the UO MSI program of 2015, for the coordination of the experiments ionizing radiation experiments at the Gamm Irradiation Facility (GIF).

Appendix





The ANOVA and t-test for the M_c as a function of temperature for all the dose-rates. The corner portions of the diamonds indicate the 5% confidence level, there for if that overlap in this region you can still indicate they are different to a 95% confidence. If not, there is a 99.99% that these two are different data sets according to the anova. The t-test is also indicative where overlap represents overlap in the spread of the data. Statistics determined using JMP software.

References

1. DOE, "Nuclear Material Packaging Manual". DOE M 441.1-1, https://www.directives.doe.gov/directives/current-directives/441.1-DManual-1/view

2. Eric M. Weis (MST-7), Cynthia F. Welch (MST-7), Paul H. Smith (NPI-2), Michael W. Blair (MST-7), Tim A. Stone (NPI-2), D. Kirk Veirs (MET-1), Kirk P. Reeves (NPI-2), Tristan Karns (NPI-2), Jude M. Oka (NPI-2), Jennie Keller (MST-7), Linda Meincke (MST-7), Joseph A. Torres (MST-7), Matthew J. Herman (MST-7), Brian Weaver (CCS-6), Jillian C. Adams (MST-7), Olivia C. Trautschold (MST-7), "Lifetime Extension Report," Los Alamos National Laboratory. (2016).

3. Flory, P. J., & Rehner, J. (1943). Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. The Journal of Chemical Physics, 11(11), 521-526. doi:10.1063/1.1723792

4. Okabe, M., Wada, R., Tazaki, M., & Homma, T. (2003). The Flory-Huggins Interaction Parameter and Thermoreversible Gelation of Poly(vinylidene fluoride) in Organic Solvents. Polymer Journal, 35(10), 798-803. doi:10.1295/polymj.35.798

5. *The Effects of Nuclear Weapons*, Revised ed., US DOD 1962, pp. 592–593.