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Thermogravimetric Characterization of Glovebox Gloves

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Thermogravimetric Characterization of Glovebox Gloves

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Thermogravimetric Characterization of Glovebox Gloves

An experimental project was initiated to characterize mass loss when heating different polymer glovebox glove material samples to three elevated temperatures, 90, 120, and 150 °C. Samples from ten different polymeric gloves that are being considered for use in the tritium gloveboxes were tested. The intent of the study was to determine the amount of material lost. These data will be used in a subsequent study to characterize the composition of the material lost. One goal of the study was to determine which glove composition would least affect the glovebox atmosphere stripper system. Samples lost most of the mass in the initial 60 minutes of thermal exposure and as expected increasing the temperature increased the mass loss and shortened the time to achieve a steady state loss. The most mass loss was experienced by Jung butyl-Hypalon® at 146°C with 12.9 % mass loss followed by Piercan Hypalon® at 144°C with 11.4 % mass loss and Jung butyl-Viton® at 140°C with 5.2% mass loss. The least mass loss was experienced by the Jung Viton® and the Piercan polyurethane. Unlike the permeation testing (1) the vendor and fabrication route influences the amount of gaseous species that is evolved. Additional testing to characterize these products is recommended.

Savannah River Site (SRS) has many gloveboxes deployed in the Tritium Facility. These gloveboxes are used to protect the workers and to ensure a suitable environment in which to handle tritium gas products. The gas atmosphere in the gloveboxes is purified using a stripper system. The process gas strippers collect molecules that may have hydrogen or its isotopes attached, e.g., waters of hydration, acids, etc. Recently, sulfur containing compounds were detected in the stripper system and the presence of these compounds accelerates the stripper system's aging process. This accelerated aging requires the strippers to be replaced more often which can impact the facility's schedule and operational cost

It was posited that sulfur bearing and other volatile compounds were derived from glove off-gassing. Due to the large number of gloves in the facility, small mass loss from each glove could result in a significant total mass of undesirable material entering the glovebox atmosphere and subsequently the stripper system. A thermogravimetric analysis (TGA) study was conducted to determine the amount of low temperature volatiles that may be expected to offgas from the gloves. The data were taken on relatively small samples but are normalized with respect to the sample's surface area. Additional testing is needed to determine the composition of the off-gassing species. The TGA study was conducted to ascertain the magnitude of the issue and to determine if further experimentation is warranted or necessary.

As part of the characterization of glovebox gloves, ten gloves from 4 different vendors were obtained. These gloves were analyzed on a TA Instruments TGA, Figure 1, at three elevated temperatures (90, 120, and 150 °C). The temperatures were selected based on the maximum use temperature of the gloves in addition to a potential maximum facility condition. The temperature range also accelerates the gas evolution and can shorten the exposure times. The tested samples were:

1. North 15 mil butyl glove
2. Piercan 15 mil butyl glove
3. Piercan 15 mil electrostatic butyl (ESDB) glove
4. Piercan 15 mil polyurethane (U) glove
5. Piercan 25 mil Hypalon® (Y) glove
6. Piercan 20 mil polyurethane Hypalon® (UY) glove
7. Guardian 15 mil butyl glove
8. Jung 24 mil Viton® (V or FKM) glove
9. Jung 20 mil Butyl Viton® (BV) glove
10. Jung 27.5 mil butyl Hypalon® (BH) glove

Figure 1. TA Instruments TGA used in this study

TGA samples were prepared by cutting rectangular samples that weighed nominally 20 mg from each glove; the dimensions were measured and the surface area was calculated. The sample was placed on the TGA pan, heated to the isothermal exposure temperature at a rate of 10°C/min and held for the programmed exposure time, usually between 8-10 hours. Argon at a flow rate of 40 sccm was purged through the balance and furnace tube. The mass and temperature data were recorded electronically at a frequency of 0.5 or 1 Hz and analyzed in MS Excel spreadsheets. The nominal percent weight loss, weight loss as a function of time, and the specific weight loss (mg/cm^2) were determined at the end point of the test or after a specified exposure time.

Results and Discussion

A typical thermogram for the North Butyl 15 mil glove exposed at 90°C is shown in Figure 2. The red line indicates the temperature while the blue indicates the percent weight. This sample lost approximately 0.45%, 98 µg, or 0.133 mg/cm^2. The majority of the mass loss occurs in the first 60 minutes after which the mass loss slows considerably. The data were curve fit using an exponential function as shown in Figure 3 for the North Butyl 15 mil glove at three temperatures. The basis for the exponential curve fit is empirical. Using this curve fit, a mass loss rate can be derived that can subsequently be used to predict the off-gassing rate at other temperatures. This assessment was completed for all the polymers and the rate data for the North Butyl Gloves data were plotted on an Arrhenius plot as is shown in Figure 4, the value at 1/T = 0.00335 is the room temperature predicted value.

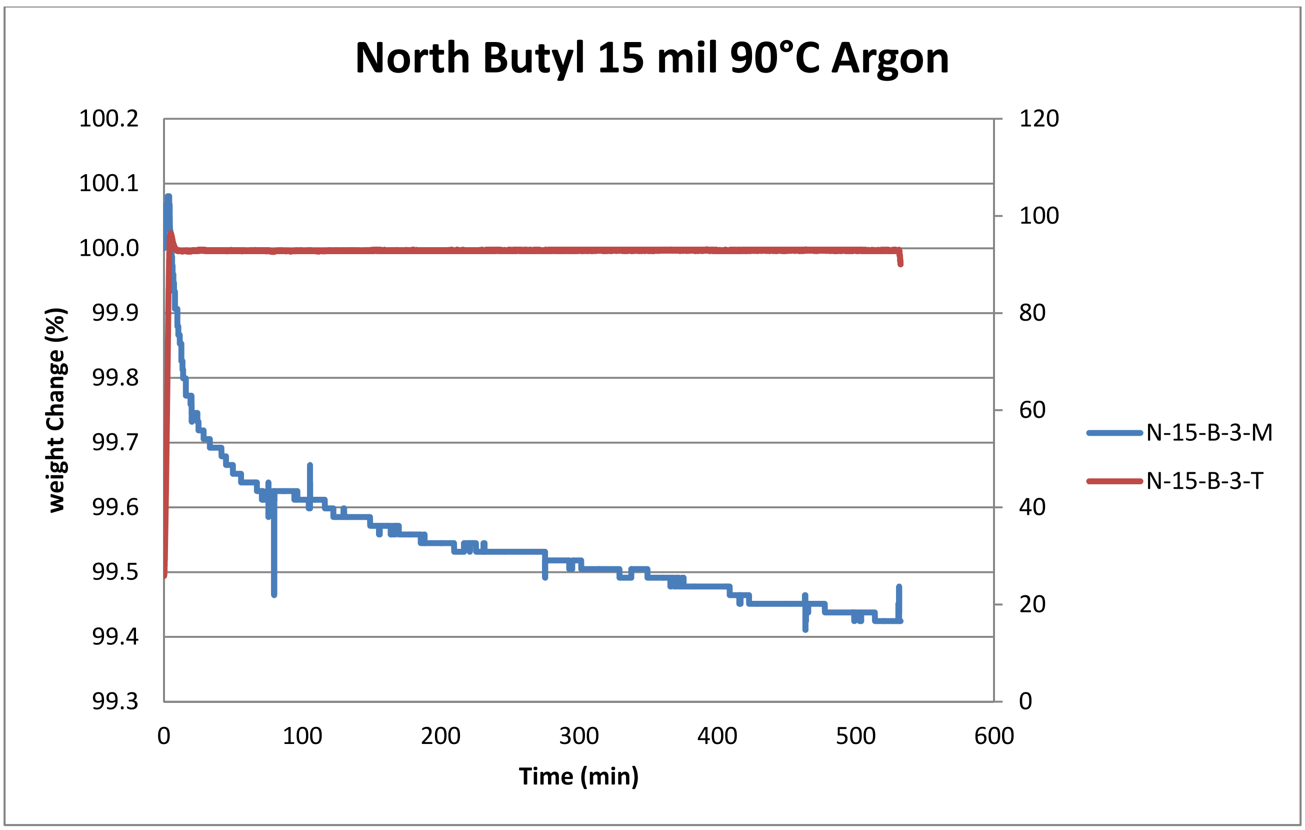


Figure 2. Piercan Butyl 15 mil 90 °C TGA- weight change versus time.

Data at the end of the test is summarized in Table 1 and lists the test temperature, duration, final mass loss %, and specific mass loss. Individual data sets plotted as a function of percent loss are presented in Appendix A while the curve fit data for the weight loss is presented in Appendix B. From a practical viewpoint, the mass loss per unit area, specific mass loss, is more useful for extrapolating to the facility. For instance, to estimate the amount of off-gas in the facility, one can use the 3375 cm^2 surface area per glove and the number of gloves, i.e., 4400 gloves, and simply multiply. This amount of material could then be expected to be evolved from the gloves after the time period for the estimate rate.

A calculated rate for each glove type can be estimated for room temperature and is shown in Table 2. It is of note that the extrapolation is somewhat different than expected based on the isothermal exposure tests. This apparent discrepancy may be attributable to a change in mechanism through the temperature range of interest. A simple specific weight change comparison for the nominal 90°C exposure temperature is provided in Figure 6. This chart shows that the North Butyl rubber, a site accepted product, exhibits about 0.1 mg/cm^2 after 300 minutes and that Guardian and Piercan Butyl rubbers, Piercan Polyurethane, and Jung Viton® and Butyl Viton® exhibit similar in mass losses or 0.1 mg/cm^2. The Piercan ESDB exhibits a specific mass loss of nearly 0.15 mg/cm^2 and Piercan Polyurethane-Hypalon® a loss of 0.19 mg/cm^2, Piercan Hypalon* 0.27 mg/cm^2 and Jung butyl-Hypalon® a loss of 0.6 mg/cm^2 for the same exposure time and temperature.

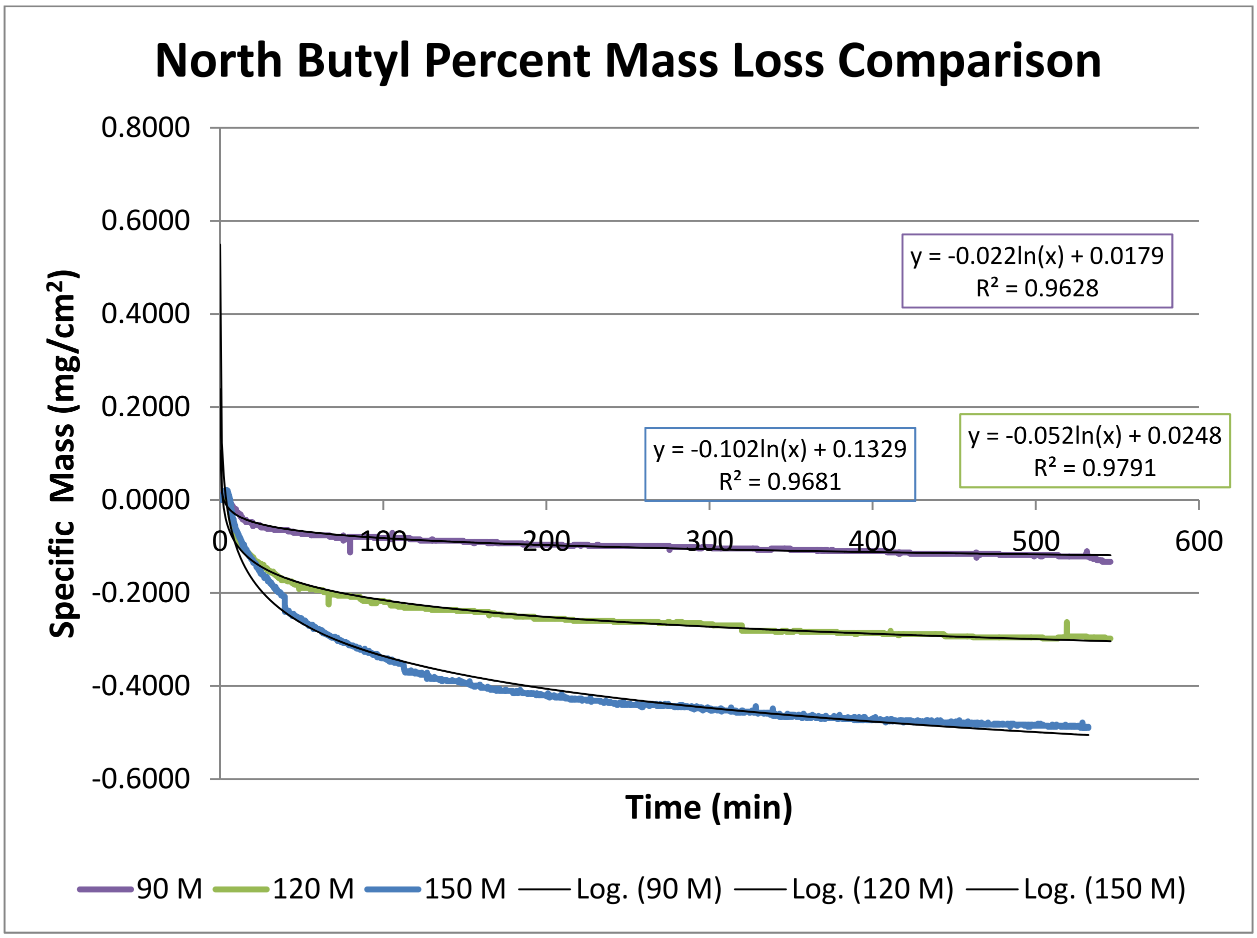


Figure 3. North Butyl data showing logarithmic curve fit of the area and the normalized data (specific mass (mg/cm^2) versus time (min)..

Table 1. Summary of Weight Change Data

TGA Test % Weight Loss				
Glove	Temp. °C	Time (Min)	% Weight Loss	Specific mass (mg/cm2)
North B15	80	536	0.9	0.19
North B15	92	493	0.7	0.15
North B15	93	526	0.6	0.12
North B15	124	546	1.4	0.30
North B15	152	533	2.5	0.49
Piercan B15	93	258	0.5	0.09
PiercanB15	90	612	0.5	0.04
Piercan B15	122	474	0.3	0.06
Piercan B15	153	546	1.2	0.21
Piercan ESDB15	92	529	1	0.16
Piercan ESDB15	123	309	1.1	0.16
Piercan ESDB15	113	546	1.7	0.27
Piercan ESDB15	147	615	1.9	0.28
Piercan ESDB15	148	519	3	0.50
Guardian B15	92	159	0.2	0.05
Guardian B15	91	612	**-0.6**	**-0.13**
Guardian B15	90	612	0.4	0.09
Guardian B15	119	511	0.6	0.13
Guardian B15	151	546	1.5	0.27
Piercan U15	96	425	0.5	0.11
Piercan U15	119	486	0.6	0.11
Piercan U15	145	518	**-0.9**	**-0.17**
Piercan Y25	91	612	1.1	0.27
Piercan Y25	113	613	1.7	0.47
Piercan Y25	144	615	11.4	2.79
Piercan UY20	91	439	0.6	0.17
Piercan UY20	92	497	0.7	0.20
Piercan UY20	119	614	1.4	0.31
Piercan UY20	150	615	5.5	1.20
Jung V24	90	523	0.2	0.08
Jung V24	121	546	0.3	0.09
Jung V24	153	511	0.4	0.14
Jung BV20	75	496	0.3	0.07
Jung BV20	115	546	2.5	0.69
Jung BV20	140	554	5.2	1.38
Jung BH27.5	85	551	1.9	0.59
Jung BH27.5	118	614	5.4	1.55
Jung BH27.5	146	615	12.9	3.70

Note: Bold values are weight gains, all other changes are losses.

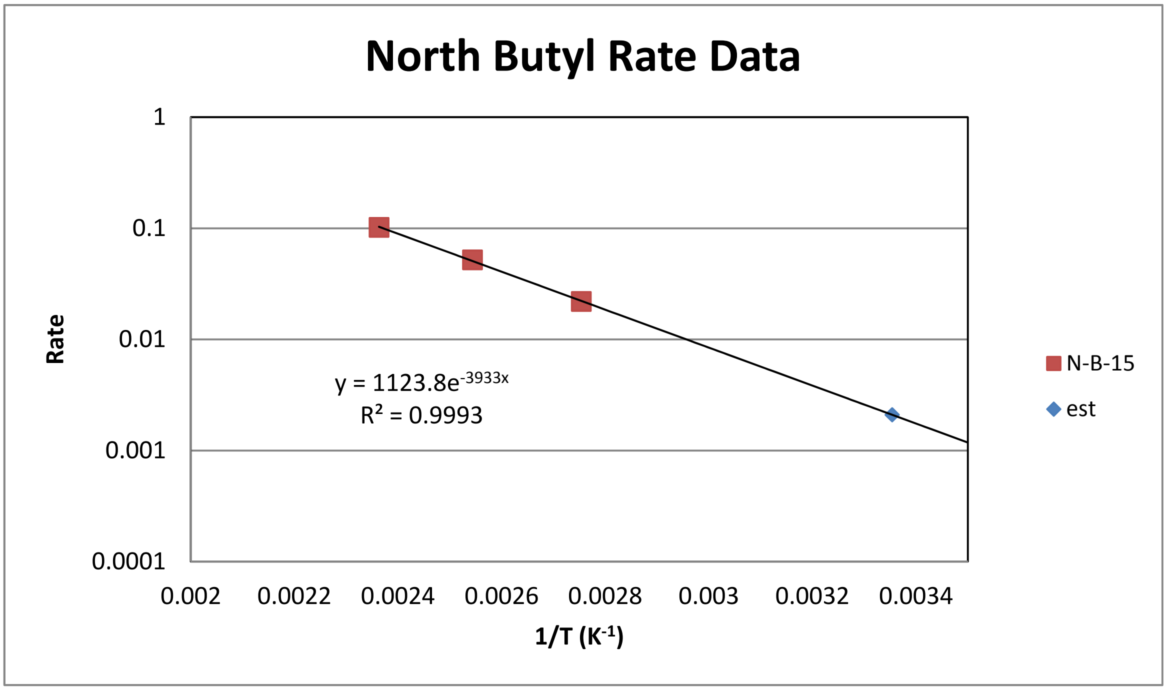


Figure 4. Arrhenius Plot of curve fit data for North Butyl Gloves

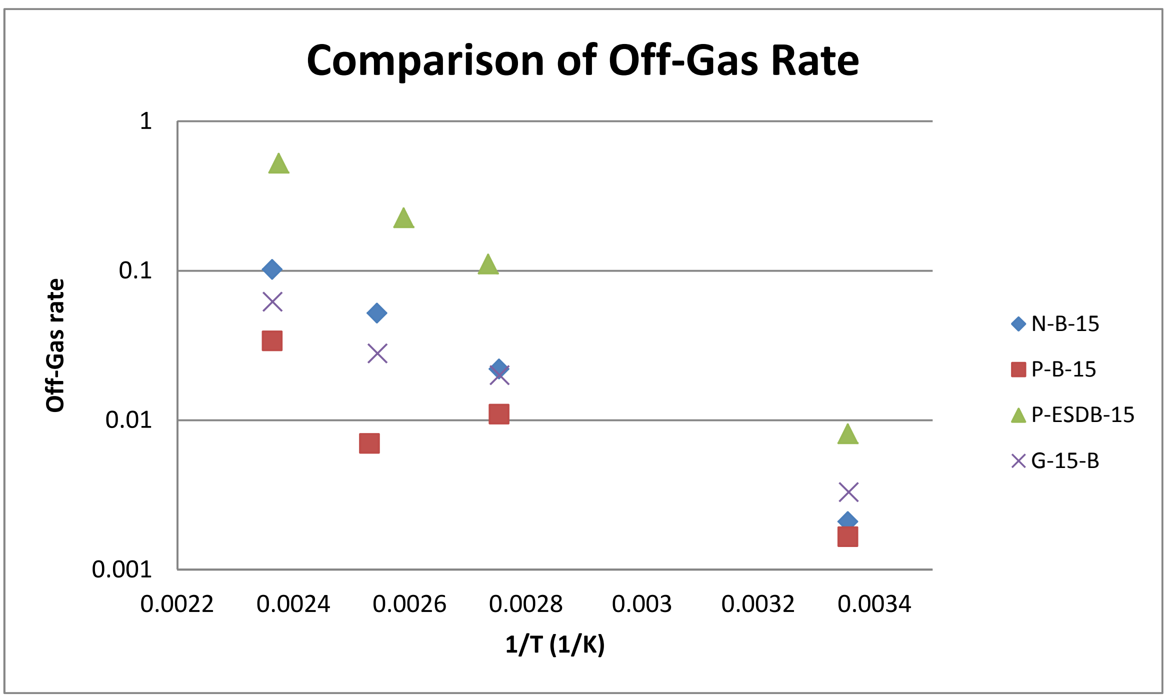


Figure 5. Calculated Off-Gas Rates for Butyl Rubber Gloves from three manufacturers.

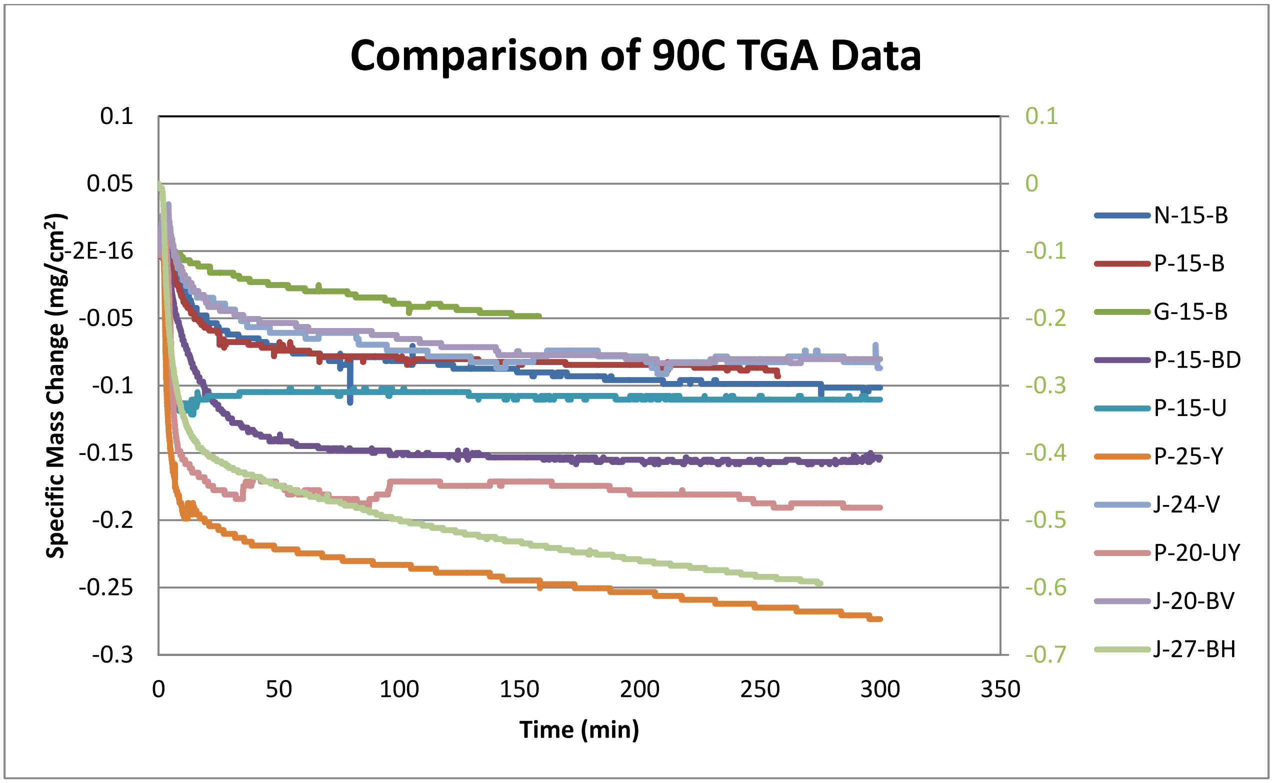


Figure 6. Comparison of TGA data for all glove samples at 90°C – Sample J-27-BH is read on the right side scale.

Summary

The largest mass losses occurred in the following samples Jung BH27.5 146°C 12.9% mass loss, Piercan Y25 144°C 11.4% mass loss, and Jung BV 140°C 5.2% mass loss, or 3.70 mg/cm^2, 2,79 mg/cm^2, and 1.38 mg/cm^2,, respectively. The gloves that showed the least amount of off-gassing were the Jung V24 and the Piercan U15. Neither of them exhibited greater than a 0.6% mass loss. For the butyl gloves Guardian B15 and Piercan B15 showed the least off gassing, staying below 0.8% mass loss. The North B15 and the Piercan ESDB15 showed a higher amount of off-gassing from 0.5 to around 3.0% mass loss. The Piercan production is considering changing over their manufacturing line to this new electrostatic butyl and the amount of off gassing will increase; however, as these ranges fall within the current off gas values of the gloves in the facility (North B15) they may be viable product.

The Piercan polyurethane gloves were tested beyond the manufacturer's recommended use temperature when exposed to 150°C. The sample was permanently deformed after testing. The weight gain is likely due to oxidation of the sample despite being tested in an argon atmosphere; other work has demonstrated that the argon purge does not completely eliminate the residual air.

During the course of this experiment, there was no way to analyze the chemical makeup of the gas that is coming off of the polymers. A projected cost analysis has been performed for an experiment that will analyze the actual make-up of the gas; this series of experiments is planned provided adequate funding can be secured.

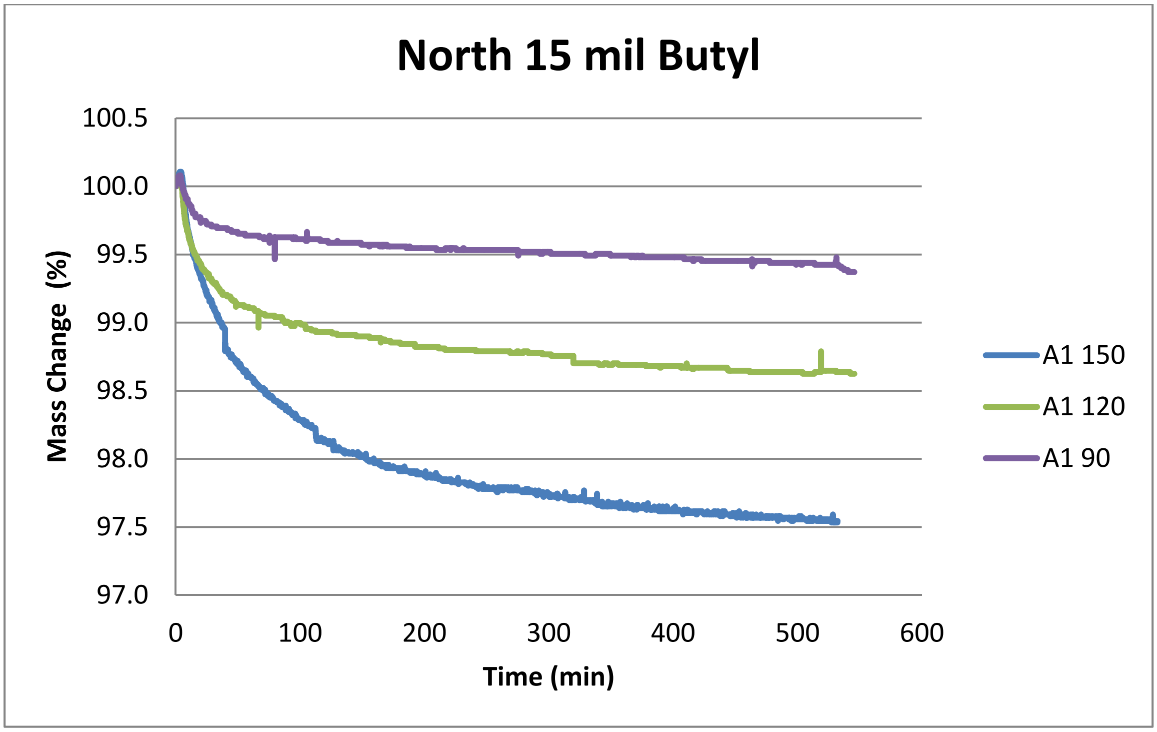
Acknowledgements

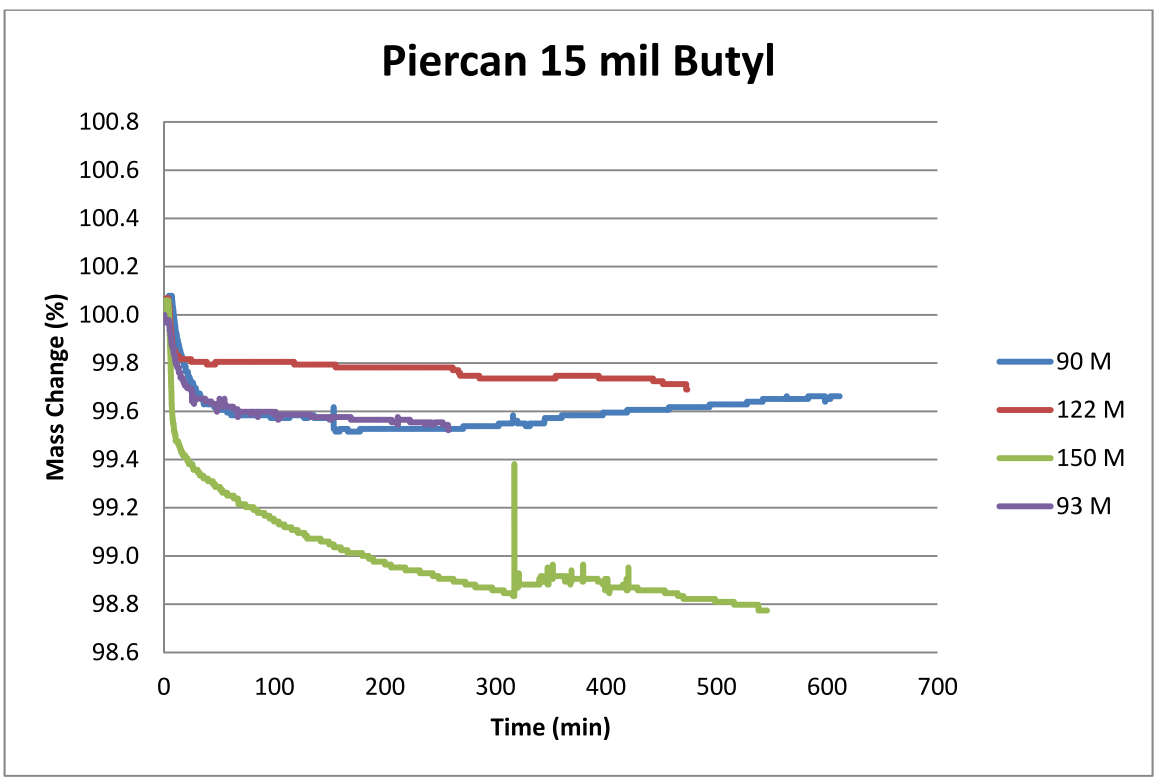
The authors would like to acknowledge Tritium Engineering and Tritium Programs for sponsoring this work.

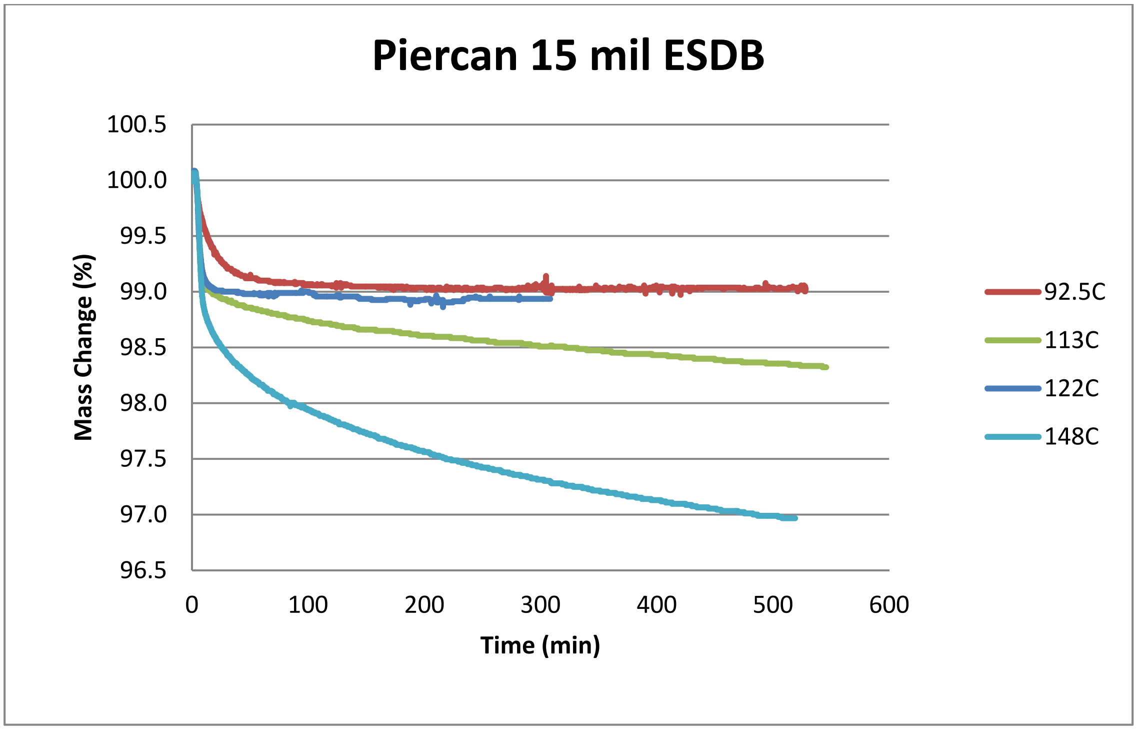
References

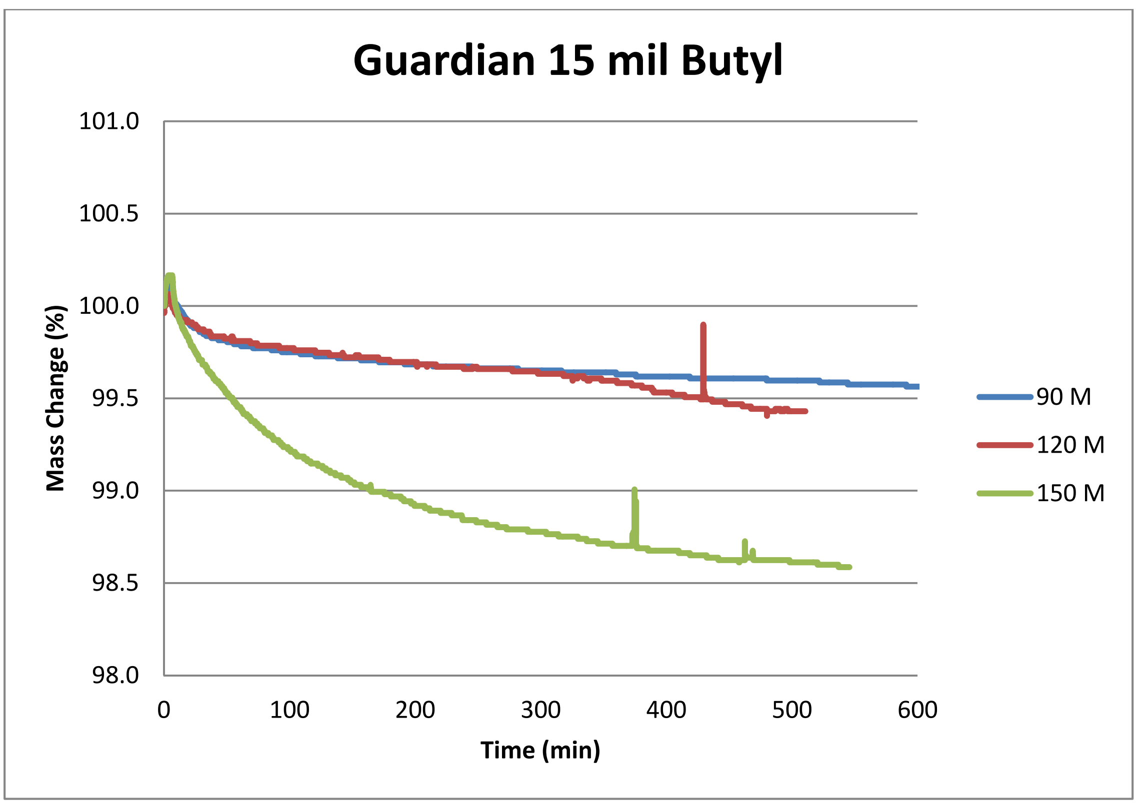
(1) SRNL-STI-2012-00028, Evaluation of Glovebox Gloves for Effective Permeation Control, P.S. Korinko and Y. Breakiron, Feb 2012

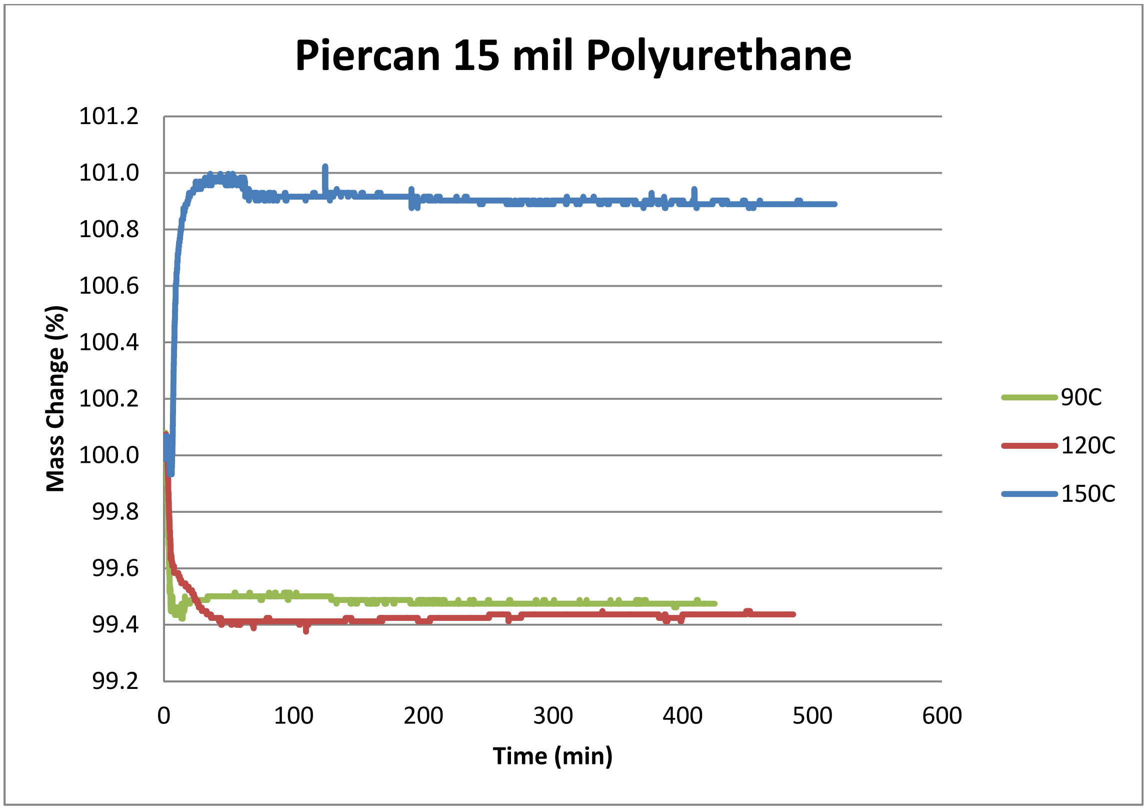
Appendix A: TGA Specific Mass Loss and Isotherm Graphs.

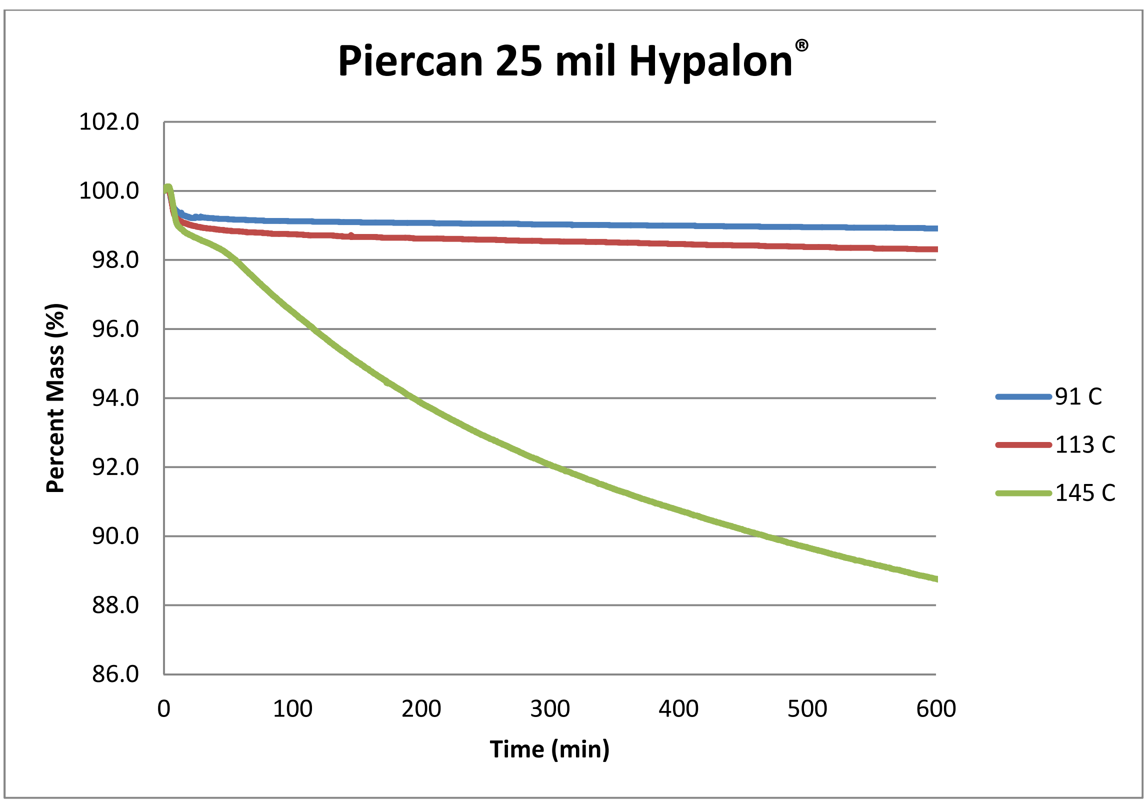


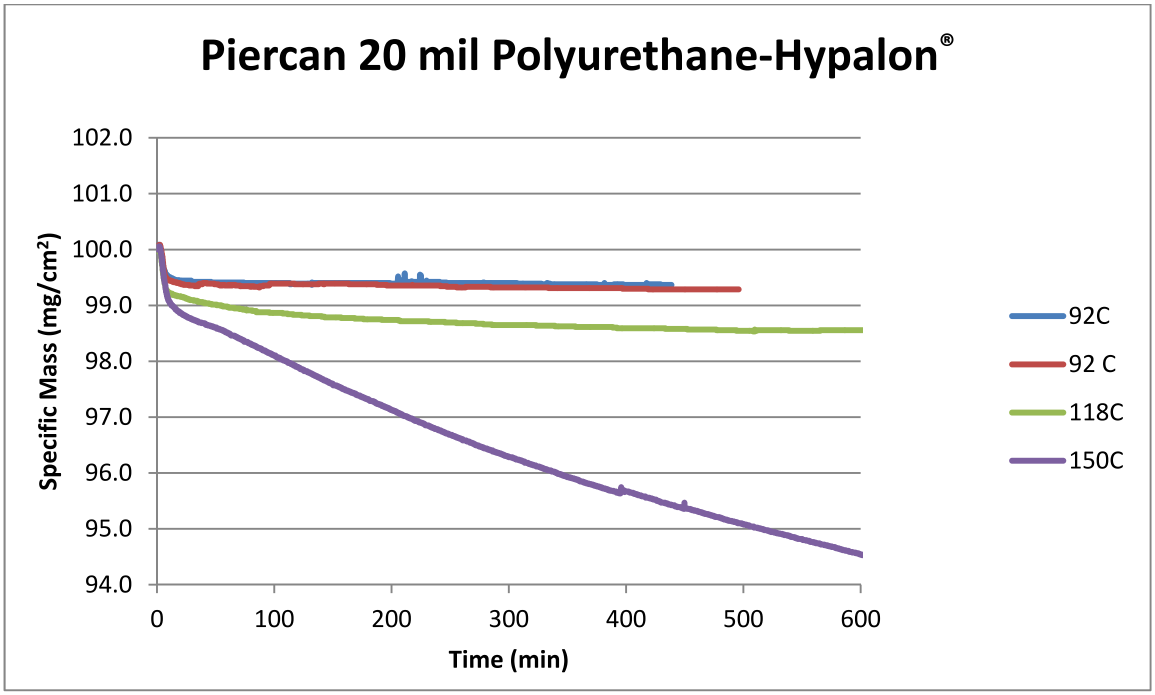


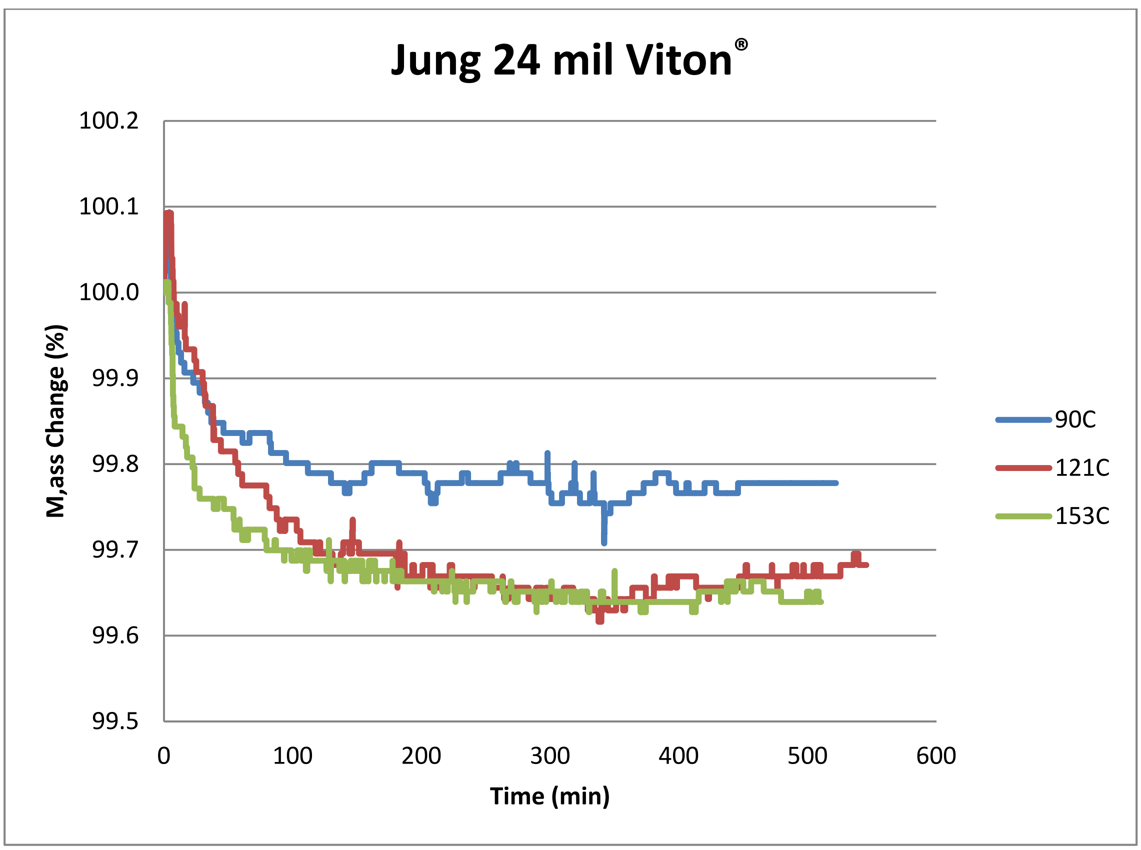

Piercan 15 mil ESDB
100.5
100.0
99.5
99.0
98.5
98.0
97.5
97.0
96.5
Mass Change (%)
0
100
200
300
400
500
600
Time (min)
92.5C
113C
122C
148C

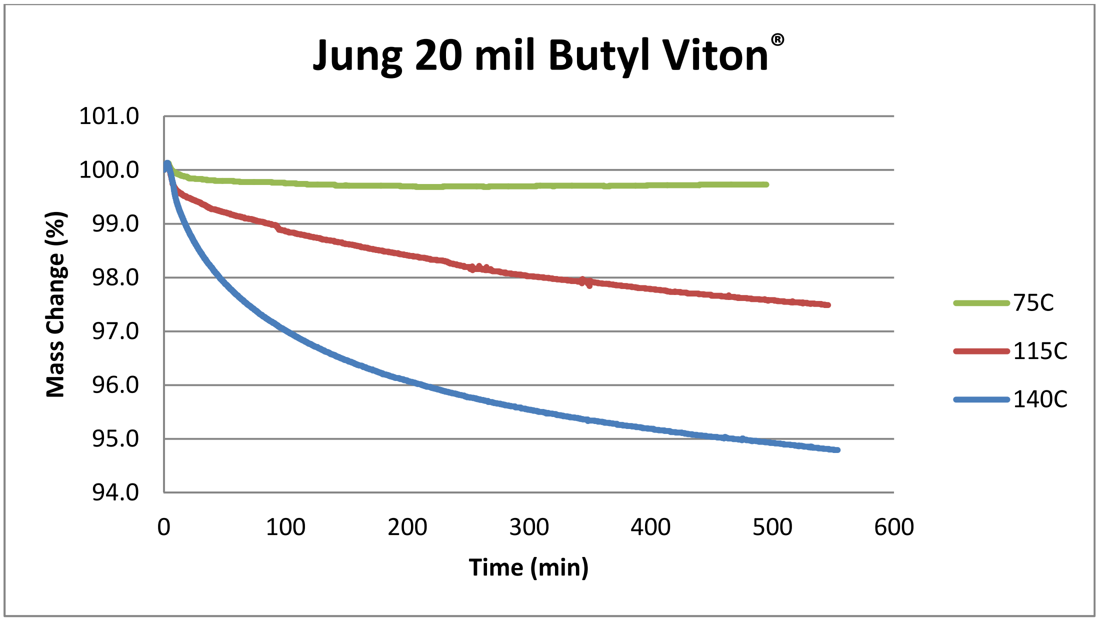

Guardian 15 mil Butyl
101.0
100.5
100.0
99.5
99.0
98.5
98.0
Mass Change (%)
0
100
200
300
400
500
600
Time (min)
90 M
120 M
150 M

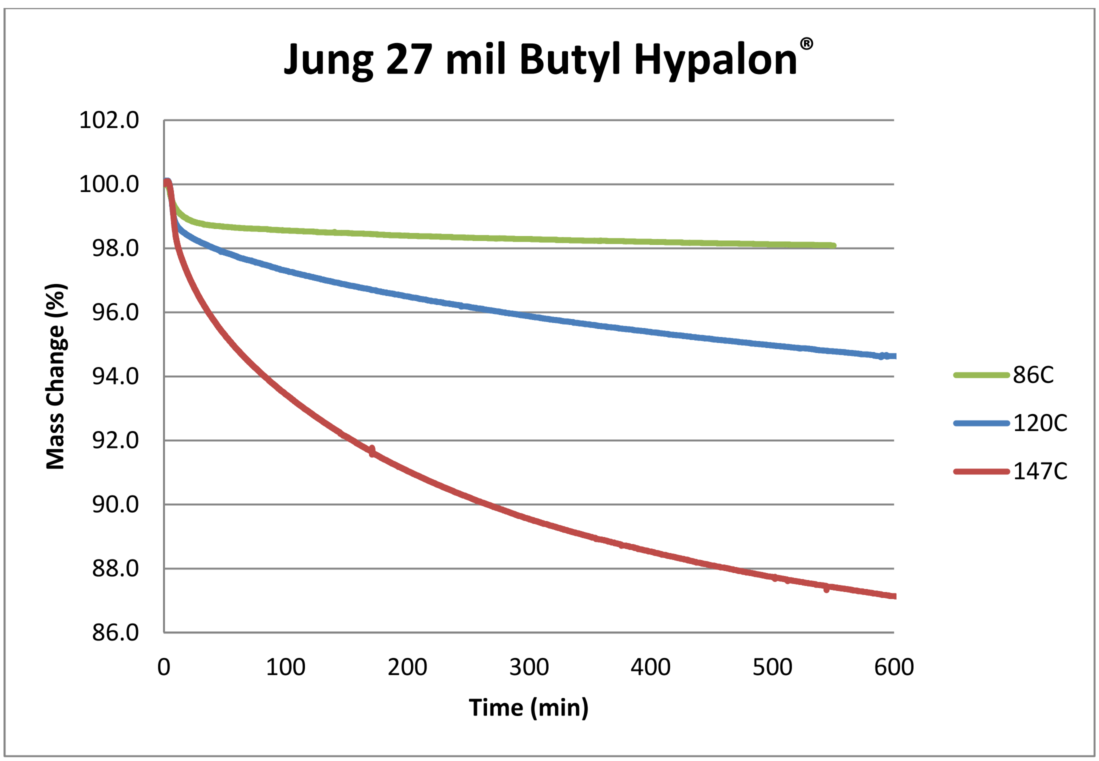

Piercan 15 mil Polyurethane
Mass Change (%)
101.2
101.0
100.8
100.6
100.4
100.2
100.0
99.8
99.6
99.4
99.2
0
100
200
300
400
500
600
Time (min)
90C
120C
150C


Piercan 25 mil Hypalon®
Percent Mass (%)
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
0
100
200
300
400
500
600
Time (min)
91 C
113 C
145 C

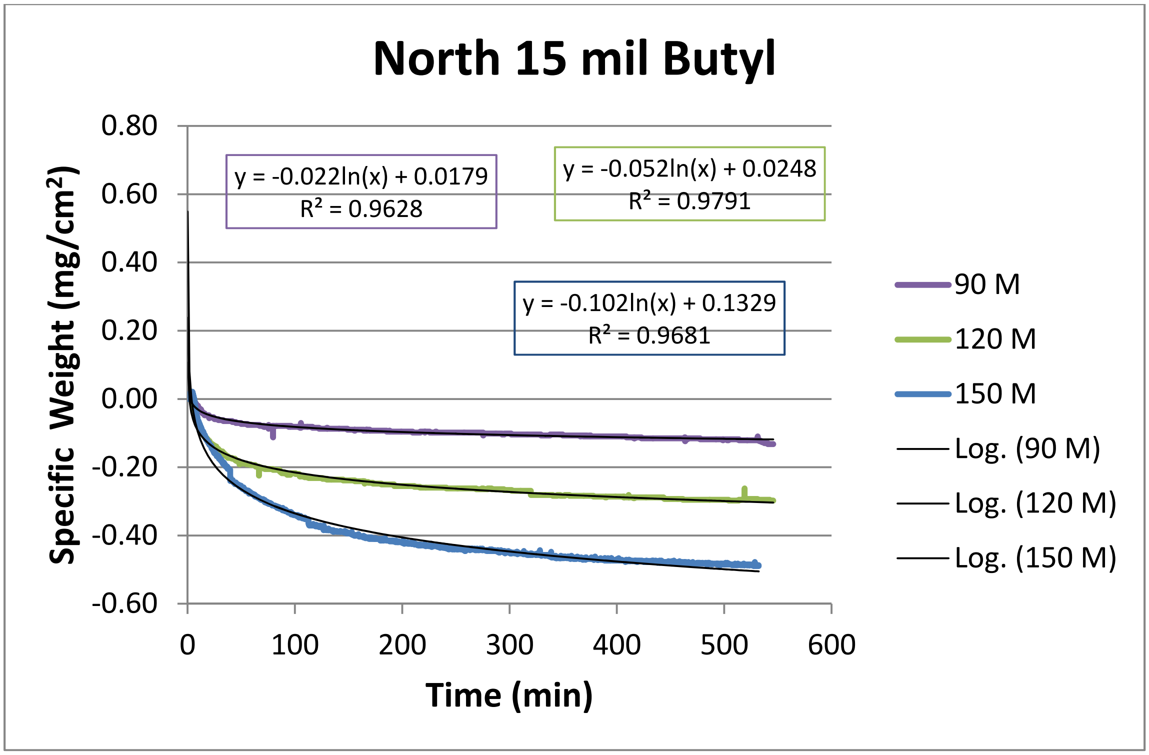

Piercan 20 mil Polyurethane-Hypalon®
102.0
101.0
100.0
99.0
98.0
97.0
96.0
95.0
94.0
Specific Mass (mg/cm²)
0
100
200
300
400
500
600
Time (min)
92C
92 C
118C
150C

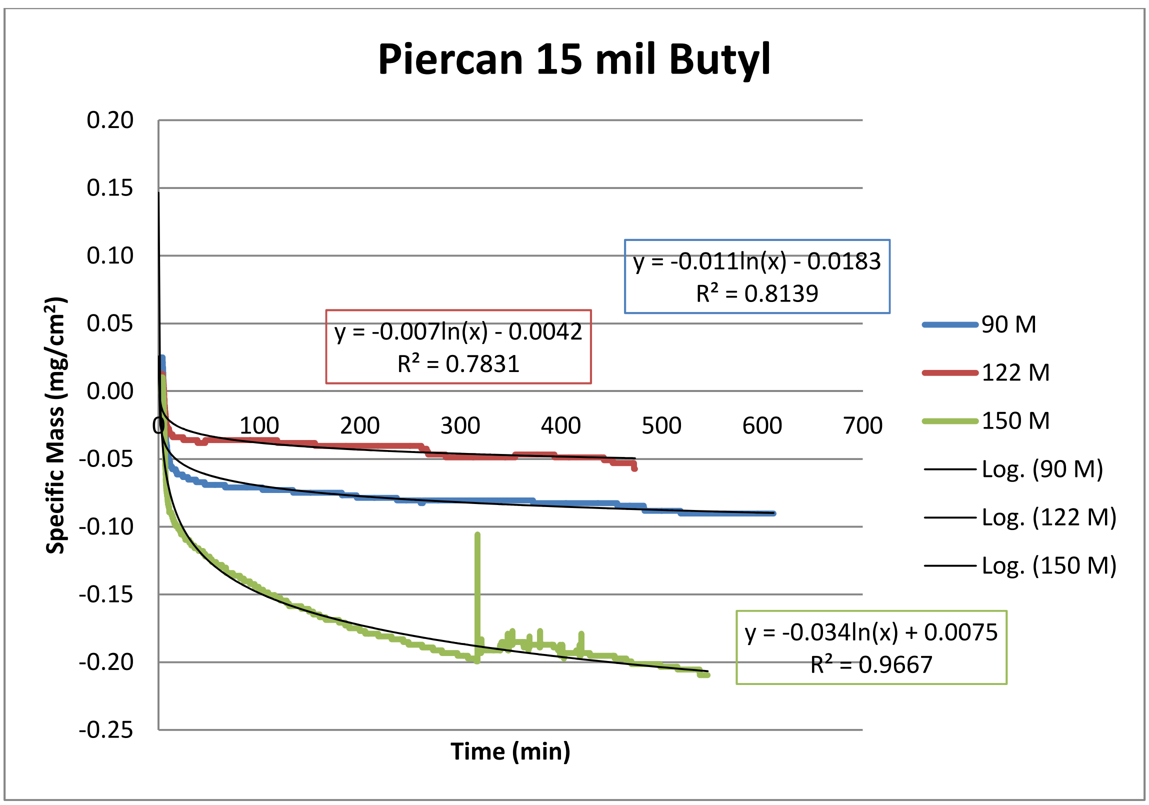

Jung 24 mil Viton®
100.2
100.1
100.0
99.9
99.8
99.7
99.6
99.5
M,ass Change (%)
0
100
200
300
400
500
600
Time (min)
90C
121C
153C

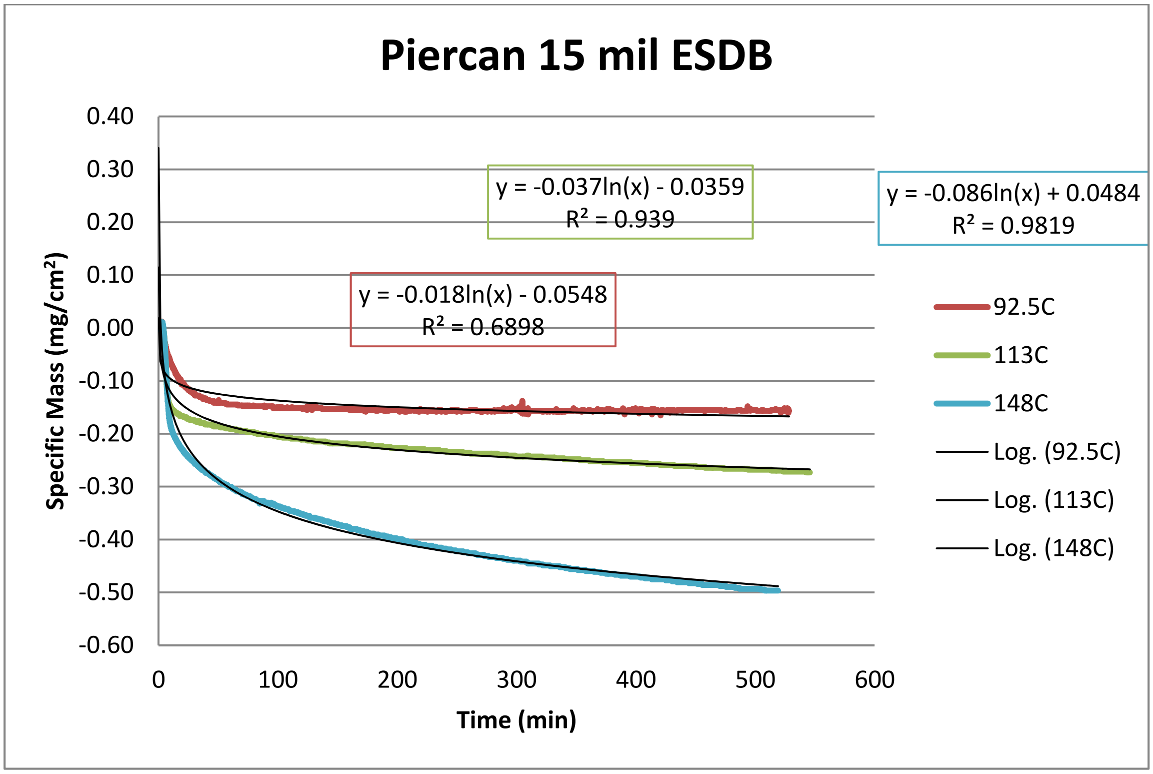

Jung 20 mil Butyl Viton®
101.0
100.0
99.0
98.0
97.0
96.0
95.0
94.0
Mass Change (%)
0
100
200
300
400
500
600
Time (min)
75C
115C
140C

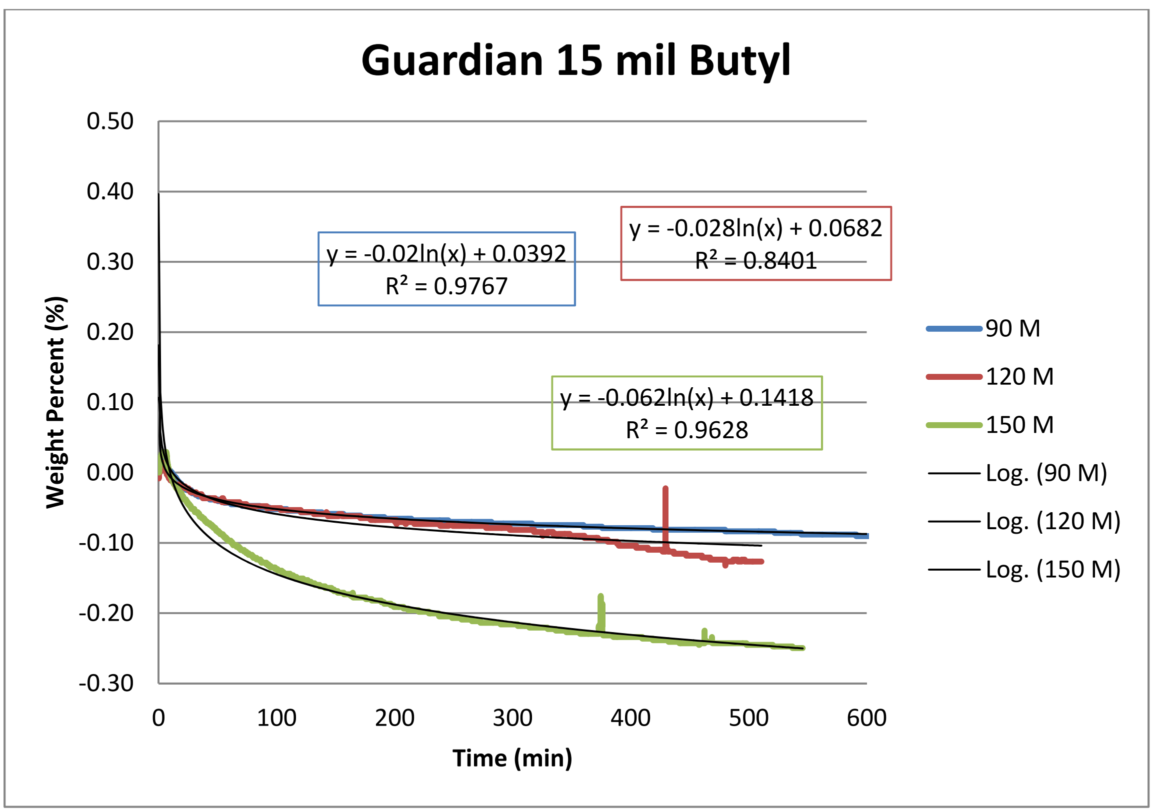

Jung 27 mil Butyl Hypalon®
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
Mass Change (%)
0
100
200
300
400
500
600
Time (min)
86C
120C
147C

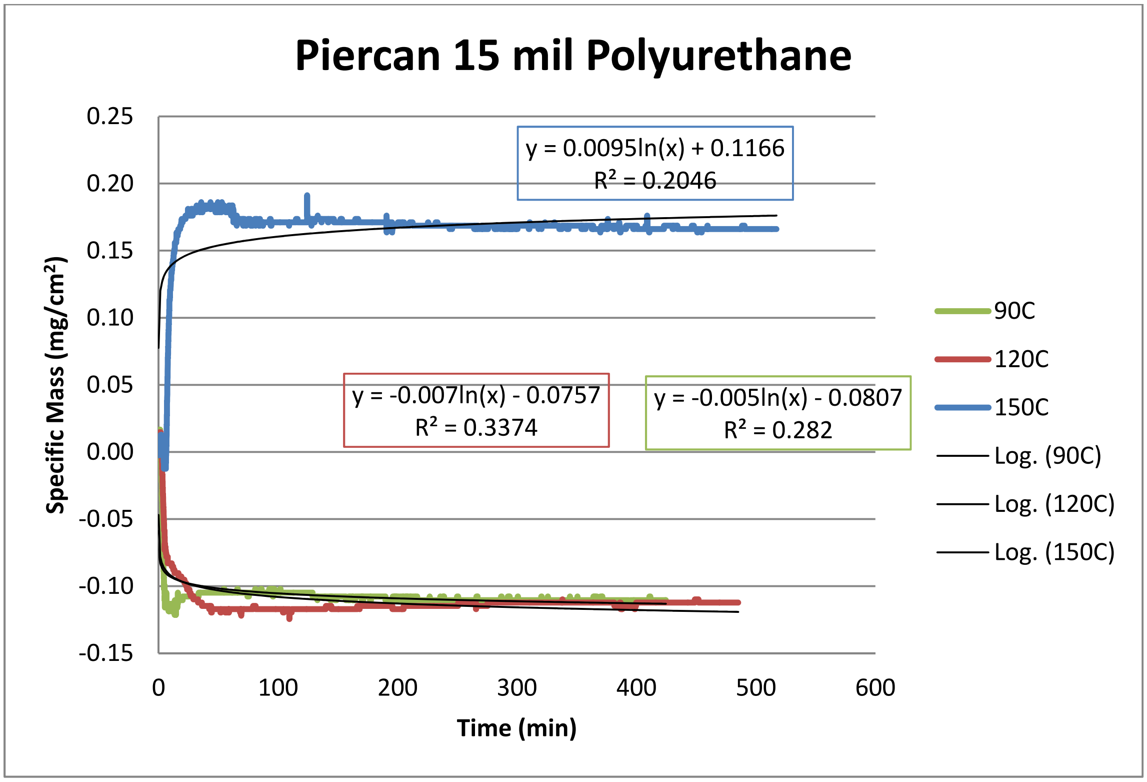
Appendix B. Specific Mass Change and Curve fit data.

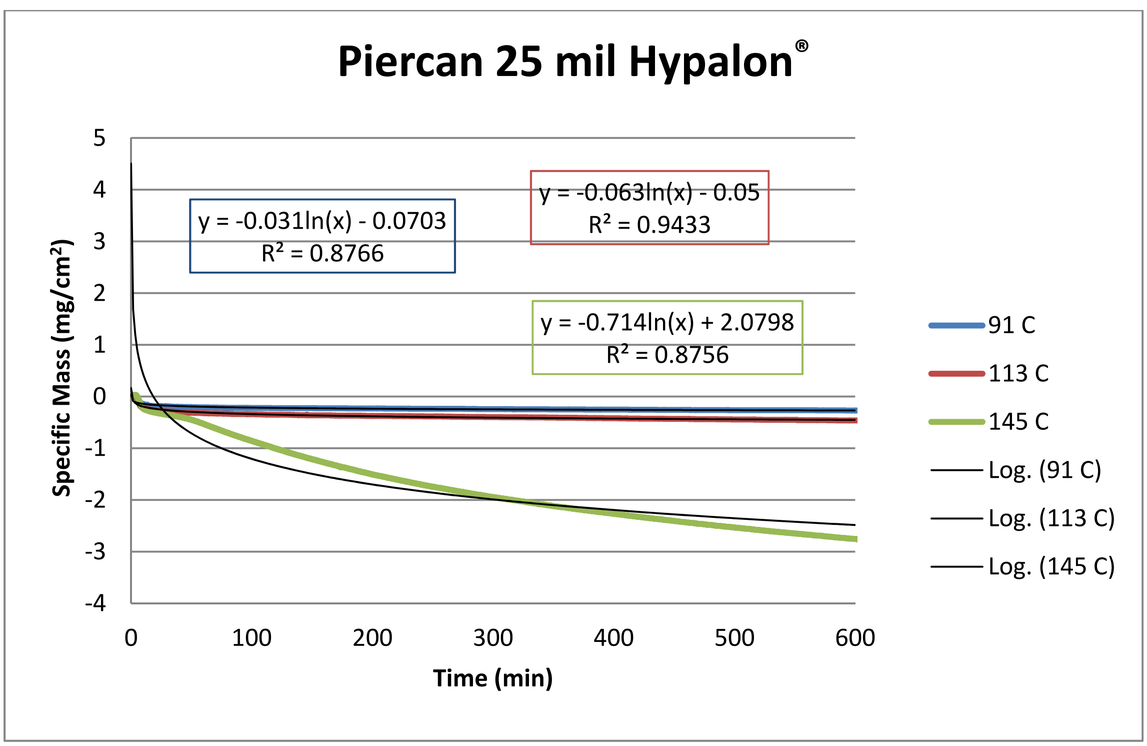


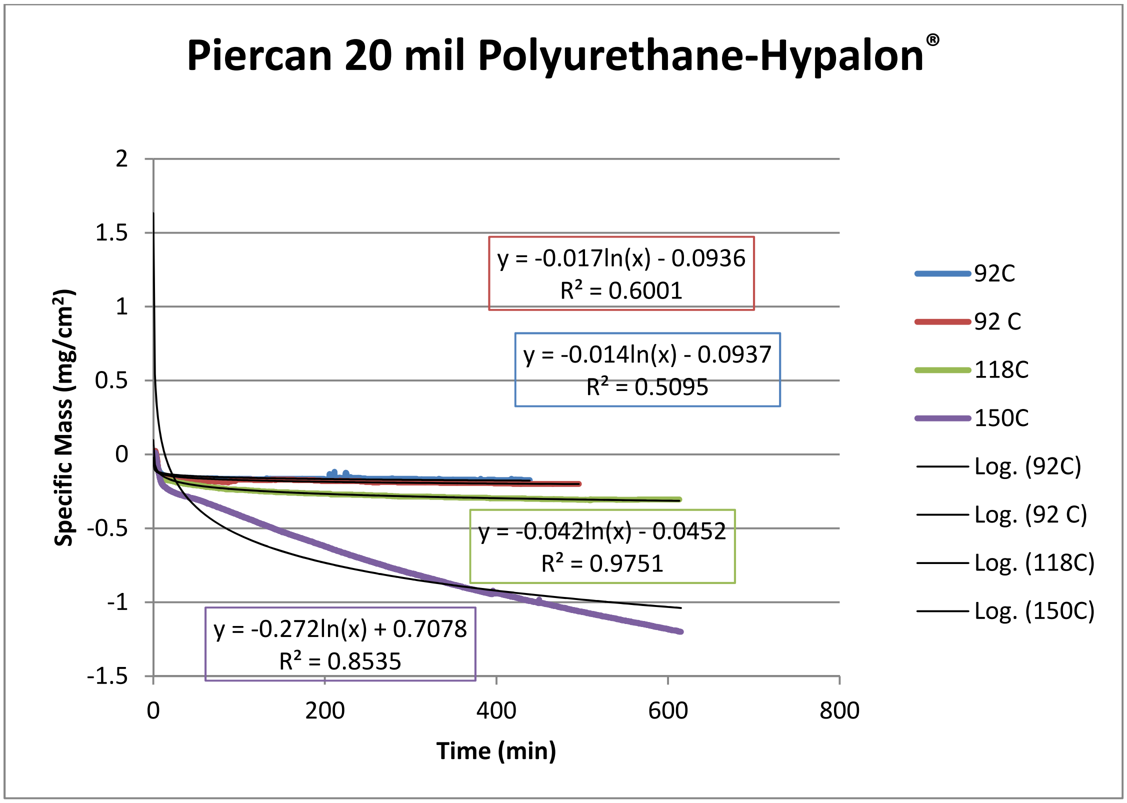


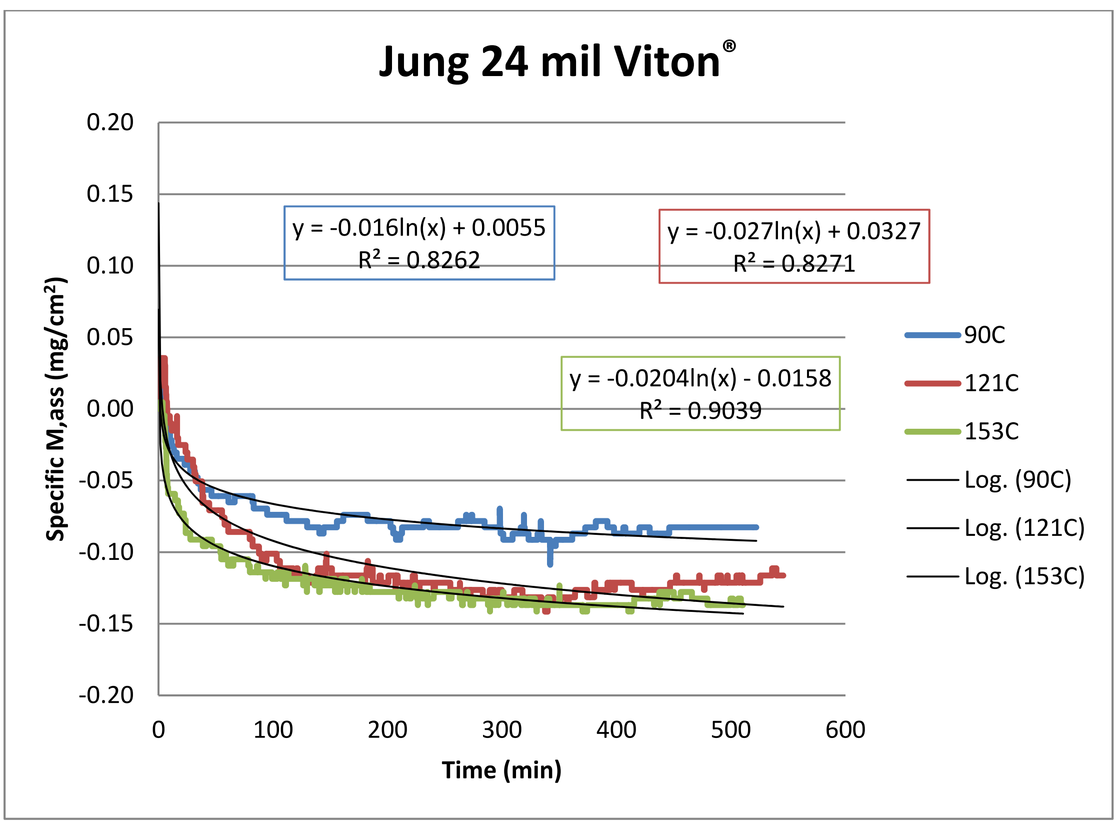

Piercan 15 mil ESDB
Specific Mass (mg/cm²)
0.40
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
-0.40
-0.50
-0.60
0
100
200
300
400
500
600
Time (min)
y = -0.037ln(x) - 0.0359
R² = 0.939
y = -0.086ln(x) + 0.0484
R² = 0.9819
y = -0.018ln(x) - 0.0548
R² = 0.6898
92.5C
113C
148C
Log. (92.5C)
Log. (113C)
Log. (148C)

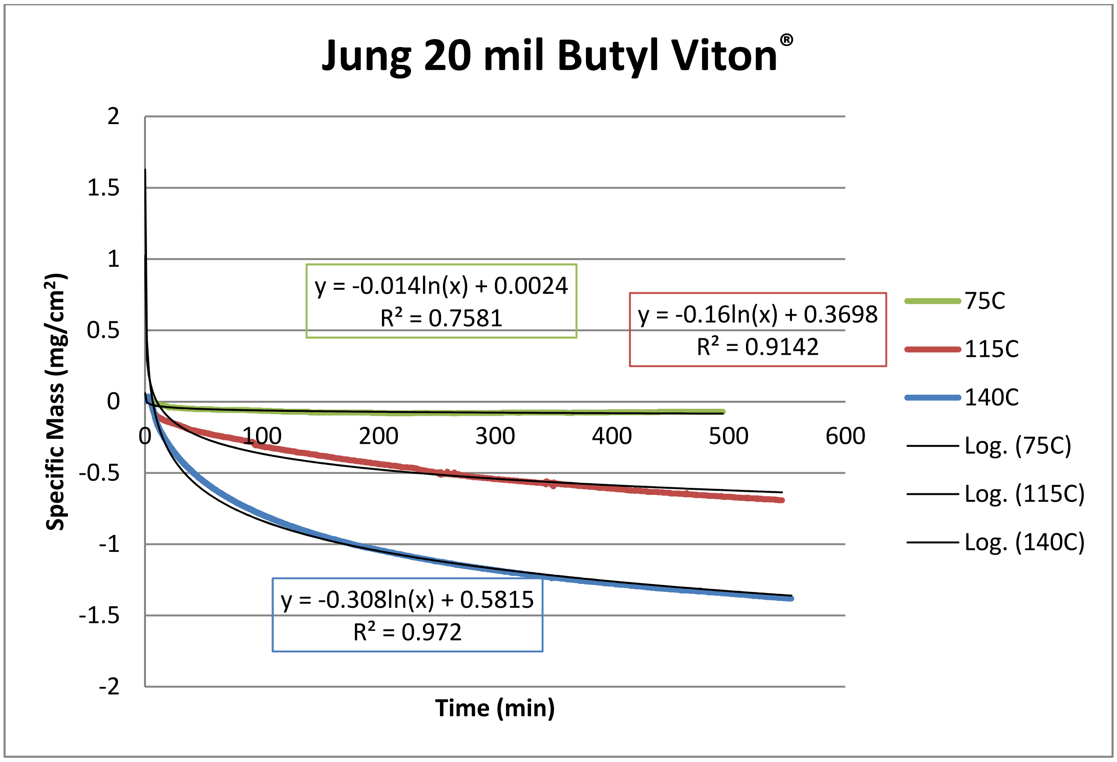

Guardian 15 mil Butyl
Weight Percent (%)
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
0
100
200
300
400
500
600
Time (min)
y = -0.02ln(x) + 0.0392
R² = 0.9767
y = -0.028ln(x) + 0.0682
R² = 0.8401
y = -0.062ln(x) + 0.1418
R² = 0.9628
90 M
120 M
150 M
Log. (90 M)
Log. (120 M)
Log. (150 M)

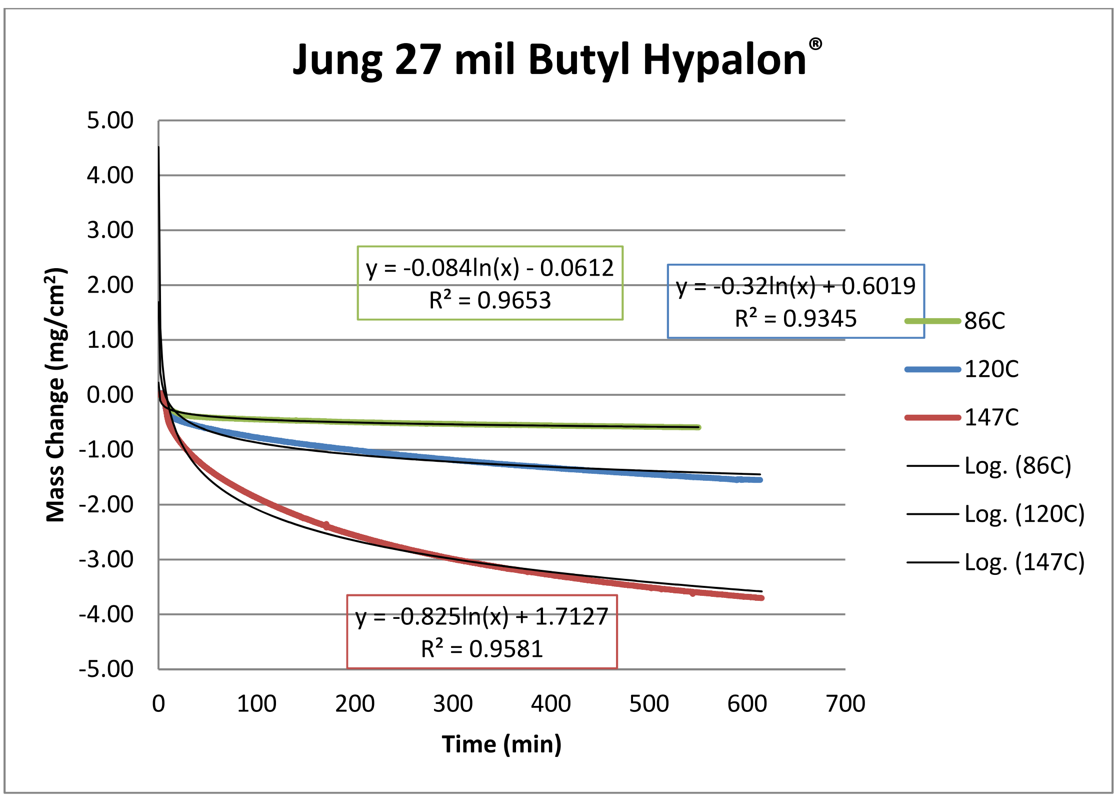

Piercan 15 mil Polyurethane
y = 0.0095ln(x) + 0.1166
R² = 0.2046
y = -0.007ln(x) - 0.0757
R² = 0.3374
y = -0.005ln(x) - 0.0807
R² = 0.282
Specific Mass (mg/cm²)
Time (min)
90C
120C
150C
Log. (90C)
Log. (120C)
Log. (150C)


Piercan 25 mil Hypalon®
y = -0.031ln(x) - 0.0703
R² = 0.8766
y = -0.063ln(x) - 0.05
R² = 0.9433
y = -0.714ln(x) + 2.0798
R² = 0.8756
Specific Mass (mg/cm²)
Time (min)
91 C
113 C
145 C
Log. (91 C)
Log. (113 C)
Log. (145 C)


Piercan 20 mil Polyurethane-Hypalon®
Specific Mass (mg/cm²)
Time (min)
2
1.5
1
0.5
0
-0.5
-1
-1.5
0
200
400
600
800
y = -0.017ln(x) - 0.0936
R² = 0.6001
y = -0.014ln(x) - 0.0937
R² = 0.5095
y = -0.042ln(x) - 0.0452
R² = 0.9751
y = -0.272ln(x) + 0.7078
R² = 0.8535
92C
92 C
118C
150C
Log. (92C)
Log. (92 C)
Log. (118C)
Log. (150C)


Jung 24 mil Viton®
Specific M,ass (mg/cm²)
Time (min)
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
0
100
200
300
400
500
600
y = -0.016ln(x) + 0.0055
R² = 0.8262
y = -0.027ln(x) + 0.0327
R² = 0.8271
y = -0.0204ln(x) - 0.0158
R² = 0.9039
90C
121C
153C
Log. (90C)
Log. (121C)
Log. (153C)


Jung 20 mil Butyl Viton®
Specific Mass (mg/cm²)
Time (min)
y = -0.014ln(x) + 0.0024
R² = 0.7581
y = -0.16ln(x) + 0.3698
R² = 0.9142
y = -0.308ln(x) + 0.5815
R² = 0.972
75C
115C
140C
Log. (75C)
Log. (115C)
Log. (140C)
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
100
200
300
400
500
600


Jung 27 mil Butyl Hypalon®
Mass Change (mg/cm²)
Time (min)
y = -0.084ln(x) - 0.0612
R² = 0.9653
y = -0.32ln(x) + 0.6019
R² = 0.9345
y = -0.825ln(x) + 1.7127
R² = 0.9581
86C
120C
147C
Log. (86C)
Log. (120C)
Log. (147C)
5.00
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
0
100
200
300
400
500
600
700