Keywords: *Gloveboxes, Polymers, Gloves, Characterization, Permeation, Puncture Testing, Tensile Testing, Thermogravimetric Analysis, Dynamic Mechanical Analysis*

Retention: *25 yrs-**10561***

SRNL-STI-2012-00147

Glovebox Glove Characterization Summary

P.S. Korinko

Y. Breakiron

March 9, 2012

We Put Science To Work™

The Savannah River National Laboratory is managed and operated for the U.S. Department of Energy by

SAVANNAH RIVER NUCLEAR SOLUTIONS, LLC

AIKEN, SC USA 29808 • SRNL.DOE.GOV

This Page Intentionally Left Blank

SRNL-STI-2012-00147

Glovebox Glove Characterization Summary

Approvals:

Signature on file 4-9-2012

____ _______________________

P. S. Korinko, Author
Materials Compatibility and Welding Technology

Signature on file 5-11-2012

____ _______________________

Y. Breakiron, Author
Tritium Engineering Intern, Clemson University

Signature on file 5-14-2012

____ _______________________

E. A. Clark, Technical Review
Materials Compatibility and Welding Technology

Signature on file 5-14-2012

____ _______________________

T. M. Adams, Manager
Materials Compatibility and Welding Technology

Table of Contents

List of Tables

List of Figures

SRNL-STI-2012-00147

Glovebox Glove Characterization Summary

Summary

A task was undertaken to determine primarily the permeation behavior of various glove compounds from four manufacturers. As part of the basic characterization task, the opportunity to obtain additional mechanical and thermal properties presented itself. Consequently, a total of fifteen gloves were characterized for permeation, Thermogravimetric Analysis, Puncture Resistance, Tensile Properties and Dynamic Mechanical Analysis. Detailed reports were written for each characterization technique used. This report contains the summary of the results.

Background

Currently, butyl gloves are used in the facility because of their low permeability; however, butyl is not a particularly tough, puncture resistant, or abrasion resistant glove. To improve the physical and mechanical properties, the butyl gloves may be used with over-gloves when exposed to wear applications. The Tritium Facility and SRS glovebox subject matter expert has been working with several vendors to characterize and improve the glove properties. Four vendors: North, Piercan, Guardian and Jung, have supplied stock and experimental glove compositions and thicknesses for engineering evaluation. The gloves from these vendors, with the composition and nominal thickness listed in Table 1, have been characterized for permeability in air and hydrogen (1) thermal decomposition using Thermogravimetric Analysis (2) Puncture Resistance (3) Tensile Properties (4) and Dynamic Mechanical Analysis (5). Details for each characterization can be found in the reference reports. This document is a brief summary of the findings of the various characterization techniques.

Table 1. Description of gloves and ID used for the testing.

Vendor	Composition	Thickness (mils)	ID		Vendor	Composition	Thickness (mils)	ID
North	Butyl	15	NB15		North	Butyl	30	NB30
Piercan	Butyl	15	PB15		Piercan	Butyl	30	PB30
Piercan	Electrostatic Discharge Butyl	15	PESDB15		Piercan	Electrostatic Discharge Butyl	24	PESDB24
Guardian	Butyl	15	GB15		Guardian	Butyl	30	GB30
Jung	Butyl-Hypalon®	27	JBH27		Jung	Butyl-Viton®	20	JBV20
Jung	Viton®	24	JV24		Jung	Viton®	31	JV31
Piercan	Polyurethane	15	PU15		Piercan	Polyurethane-Hypalon®	20	PUY20
Piercan	Hypalon®	25	PY25					

Experimental

The permeation testing was conducted on a purpose built apparatus in SRNL. Disk samples were cut from the glove sleeves and tested at subatmospheric pressures from 70 to 700 Torr at room temperature.

Thermogravimetric Analysis (TGA) was conducted using a TA Instruments TGA 951. Isothermal tests were run at 90, 120, and 150°C with argon purge gas for times up to 8 hours.

Puncture testing was conducted in agreement with ASTM D-120(6) using an Instron Model 4705 load frame including a MTS Systems Renew Package. Disks were cut from the hand portion of the glove.

Tensile testing was conducted on the same equipment as puncture testing and in agreement with ASTM D412(7) for tensile testing polymers. An extension rate of 20 in/min and a 200 lbf load cell were used.

A TA Instruments 2950 Dynamic Mechanical Analyzer was used for this study. It is a forced oscillation, non-resonant, constant amplitude instrument. A tensile clamp, or sample holder was used due to the thickness of the sample and broad temperature range of interest. Rectangular test samples were cut from each glove. Tests in triplicate were completed from about 20°C below the glass transition temperature (T_g) to the maximum vendor recommended temperature or 150°C, whichever temperature was lower.

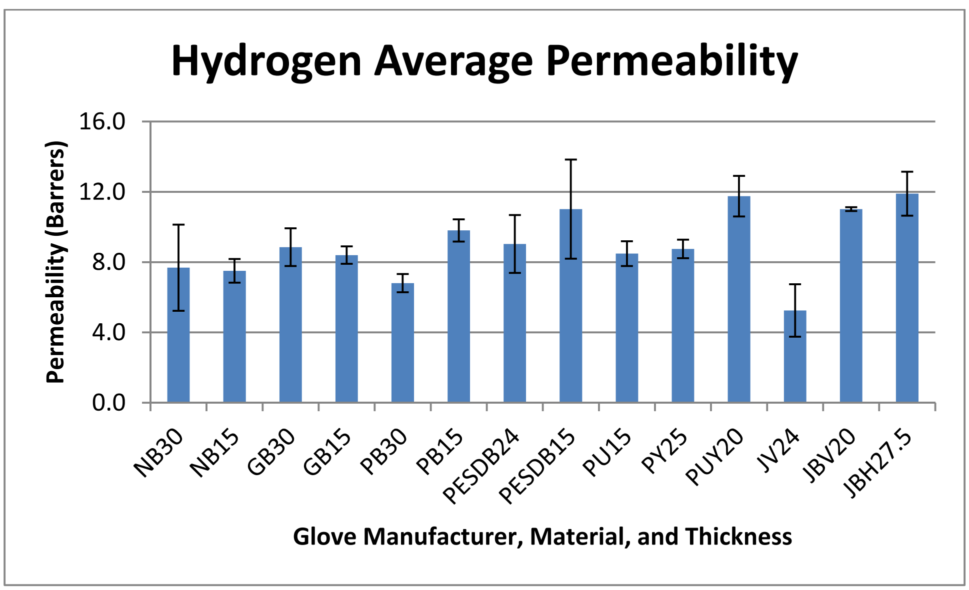

Figure 1. Hydrogen Average Permeability.

Results and Discussion

The measured permeability of hydrogen and air are indicated in Table 2, Figure 1 and Figure 2. It is apparent from these data that the room temperature permeability of the butyl rubber gloves varies between 7 and 11 barrers (10^{-10}) cc H_2 * cm / (cm^2 *cm Hg), regardless of glove manufacturer. The data in Figure 1 indicates that the permeability of butyl gloves, regardless of curing treatment, has a similar value. A statistical analysis of the hydrogen permeability indicates that all these values are consistent with each other and these determined values for the butyl rubber are consistent with literature data (1).The polyurethane and Hypalon® gloves exhibit comparable permeabilities to the butyl gloves with values of 8.5 and 8.7 barrers, respectively. The Jung Viton® glove exhibits the lowest hydrogen permeability of the materials tested with a value of about 5 barrers. This permeability value was determined to be statistically significantly lower than the butyl gloves. The composite gloves, i.e., Piercan Polyurethane-Hypalon®, Jung Butyl-Hypalon®, and Butyl-Viton®, all exhibit higher permeabilities than the pure compound gloves. The hydrogen permeability varies between 11 and 12 barrers for these compositions.

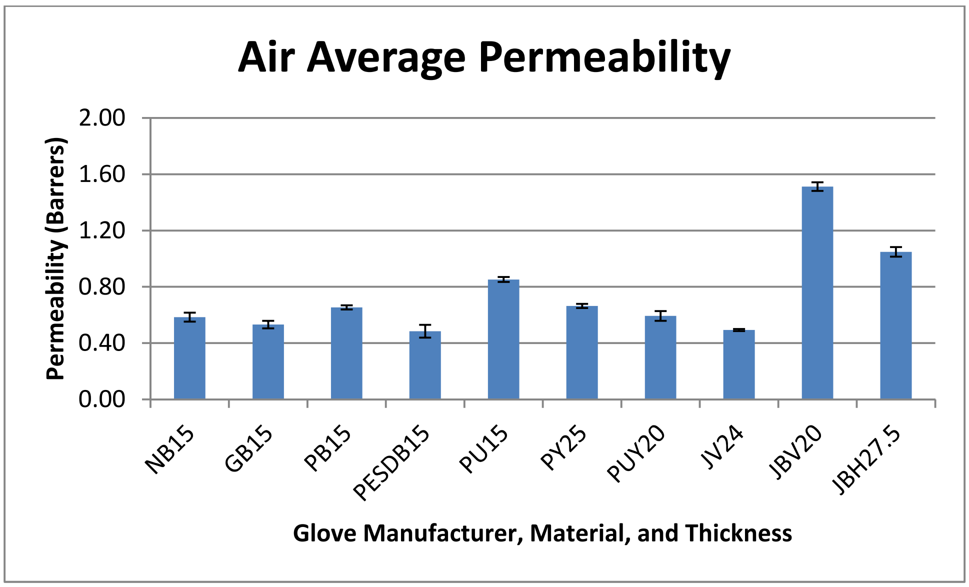

Figure 2. Air Average Permeability

The dry air permeability data, Figure 2, showed similar trends. The air permeability through each butyl glove varied between 0.48-0.65 barrers. There is not a significantly lower or higher performing glove from the butyl materials tested. The Viton® glove had a dry air permeability of about 0.49 barrers, a value at the lower end of the butyl range. The polyurethane and Hypalon® gloves were at the high end or above the Butyl rubber range, as was the Piercan polyurethane-Hypalon®. The Jung Butyl-Viton® and Jung Butyl-Hypalon® exhibited air permeabilities about twice the Butyl rubber gloves.

A more practical method to see the effect of the permeability is to examine the amount of tritium expected to permeate through the gloves. A calculation using the following assumptions and constants provides a comparative basis. A glove has a surface area of 3375 cm^2, the tritium content is 0.5 $\mu Ci/cm^3$ (2.1×10^{-7} cm^3 T_2/cm^3), the internal glovebox pressure is -0.5 in H_2O, the glove descriptions accurately reflect the nominal thickness, e.g., a North 15 mil is nominally 0.015” thick, and the glovebox and room are at 25°C. The results of this calculation are shown in Figure 3 for a 24 hour exposure using the average permeability for hydrogen that was measured for each glove. The calculations for permeation through each glove indicates that lower permeabilities result in lower overall permeation events and that thicker gloves of the same compound will exhibit lower permeation.

Table 2. Average Hydrogen and Air Permeability.

Average Permeability 10^{-10} cc H_2 * cm / (cm^2 *cm Hg) -- Barrers					Permeability *10^{-7} cc H_2 * cm / (cm^2 *atm)	
ID	H_2	Stdev.	Dry Air	Stdev.	H_2	Air
NB30	7.7	2.5	NA	NA	0.58	NA
NB15	7.5	0.67	0.58	0.03	0.57	0.044
GB30	8.9	1.1	NA	NA	0.68	NA
GB15	8.4	0.50	0.53	0.03	0.64	0.040
PB30	6.8	0.52	NA	NA	0.52	NA
PB15	9.8	0.64	0.65	0.01	0.74	0.049
PESDB24	9.0	1.6	NA	NA	0.68	NA
PESDB15	11	2.8	0.48	0.05	0.84	0.036
PU15	8.5	0.70	0.85	0.02	0.65	0.065
PY25	8.7	0.53	0.66	0.01	0.66	0.052
PUY20	12	1.2	0.59	0.03	0.91	0.044
JV24	5.2	1.5	0.49	0.01	0.39	0.037
JBV20	11	0.11	1.5	0.03	0.84	0.11
JBH27.5	12	1.3	1.0	0.03	0.91	0.076

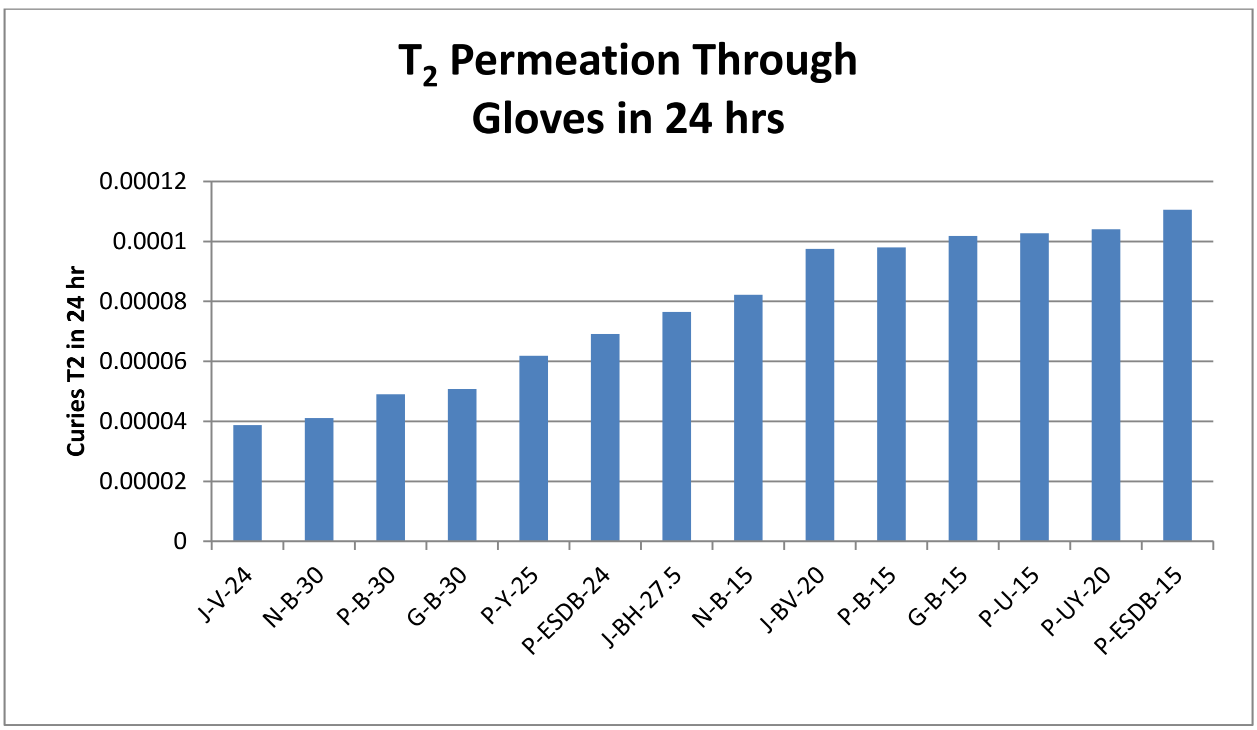

Figure 3. Graphical representation of tritium permeation in 24 hours for each glove type and thickness tested.

For the Thermogravimetric Analysis, the specific mass loss for the gloves tested at 90°C is presented in Figure 4. 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, since these ranges fall within the current off-gas values of the gloves in the facility (North B15) they may be viable product.

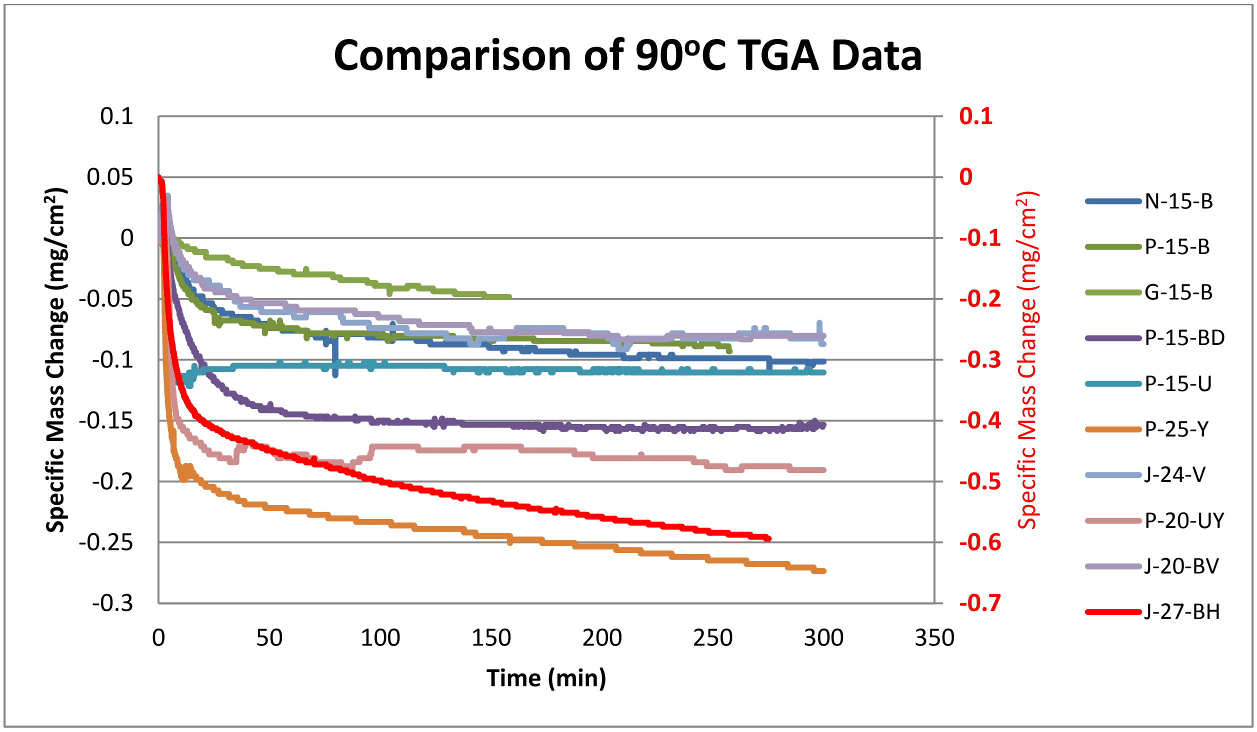

Figure 4. Specific mass change for glove samples exposed at 90°C to argon, J-27-BH is read on the right hand axis.

All of the gloves exceed the minimum puncture resistance of 100 lbf/in required for electrical gloves (6). The SRS specification does not explicitly require puncture testing, so these data are for information and comparison purposes only. The gloves can be ranked from highest to lowest puncture resistance: polyurethane, polyurethane-Hypalon®, Hypalon®, Butyl and Viton®, Butyl-Hypalon® and finally Butyl-Viton®, as shown in Figure 5.

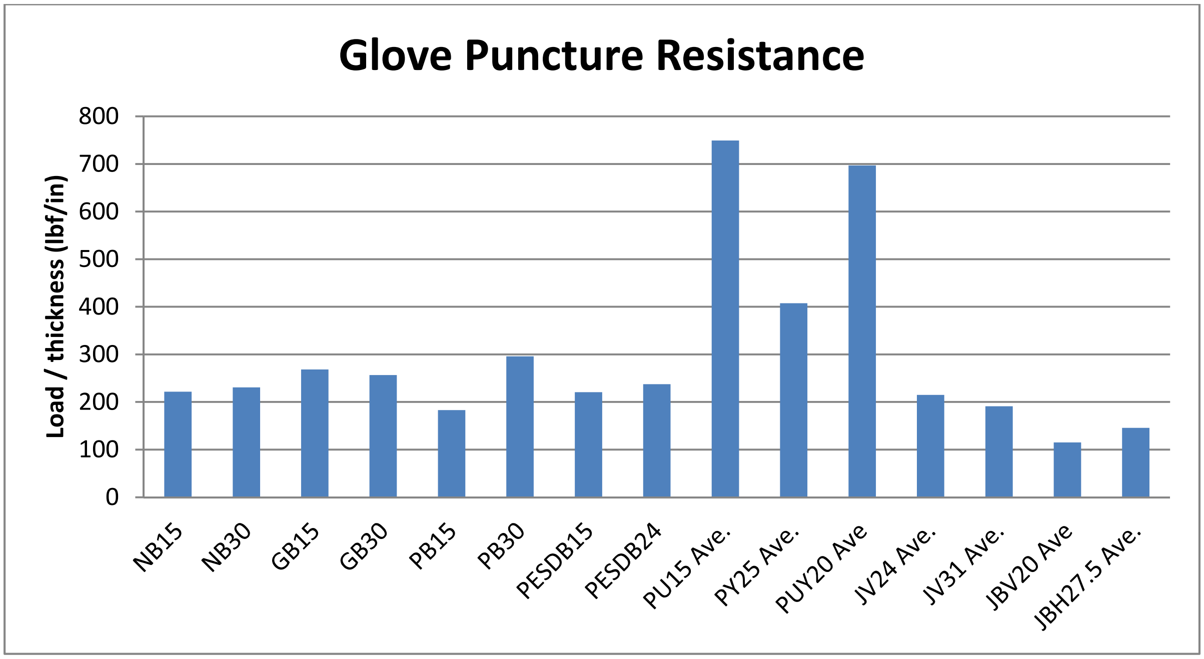

Figure 5. Puncture resistance of the gloves evaluated in this study.

Table 3. Tensile properties of the gloves tested in this study.

	GB15 Ave.	GB30 Ave.	NB15 Ave.	NB30 Ave.	PB15 Ave.	PB30 Ave.	PESDB15 Ave.	PESDB24 Ave.
Stress (Mpa)	11	12	15	13	11	11	13	13
% Elong	666	726	745	754	714	843	680	746
Load (lbf)	16	27	23	31	15	27	14	19
Thickness (in)	0.020	0.029	0.021	0.034	0.019	0.032	0.015	0.020

	JBH27 Ave.	JBV20 Ave.	JV24 Ave.	JV31 Ave.	PU15 Ave.	PUY20 Ave.	PY25 Ave.
Stress (MPa)	7.8	8.0	7.6	5.4	49	24	19
% Elong	454	640	545	453	697	603	570
Load (lbf)	16	10	14	15	55	37	30
Thickness (in)	0.045	0.017	0.025	0.039	0.015	0.022	0.021

These tensile strength (TS) results for all the gloves are listed in Table 3. The strength ranges from a low of 5.4 MPa for Viton to a high of 49 MPa for Polyurethane. The rankings are Viton® at 5.4 MPA for a 31 mil thick glove as the lowest, the butyl-Hypalon®, butyl-Viton®, and 24 mil Viton® are second lowest with about 8 MPa, then Butyl at 8-11 MPa, followed by Hypalon® at 19 MPa, Hypalon®-Polyurethane with 24 MPa and finally, Polyurethane at 49 MPa. Graphically these data can be seen in Figure 6 for both tensile strength and elongation. All of the samples exhibit at least 400% elongation with all of the butyl gloves being over 600%.

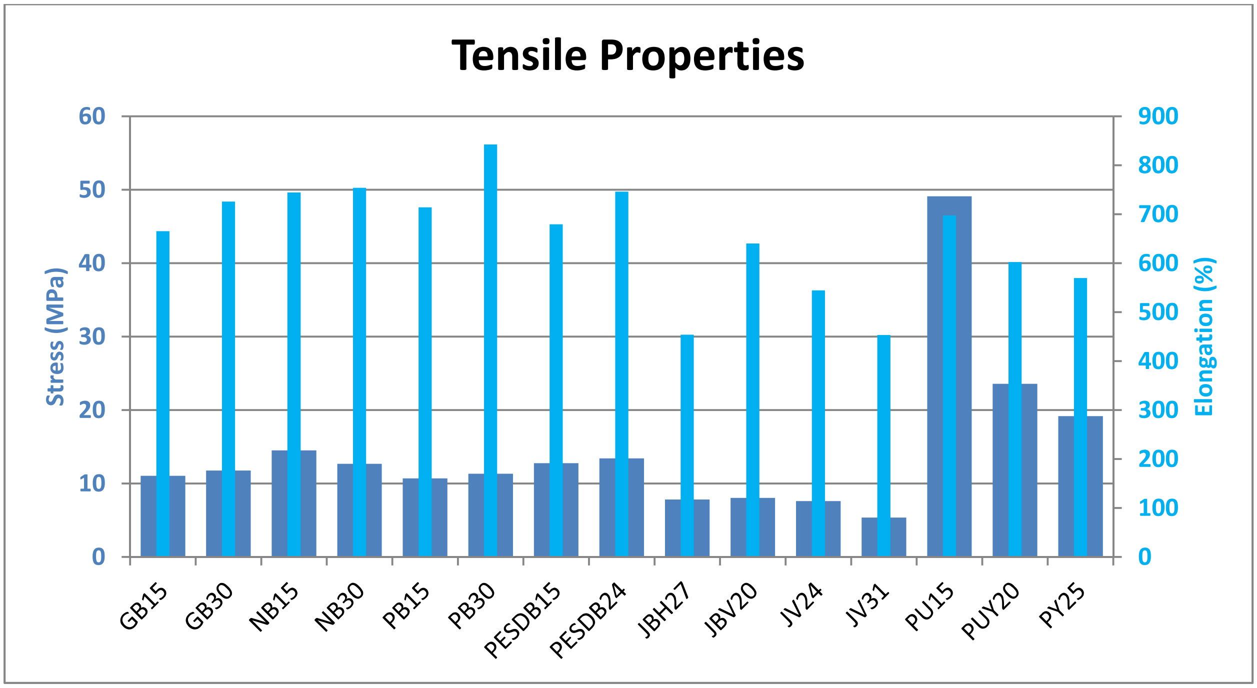

Figure 6. Tensile properties of gloves tested in this study.

Dynamic Mechanical Analysis (DMA) was also conducted on the samples. The materials were generally well behaved with storage moduli and loss moduli decreasing with increasing temperatures, with the exception of North Butyl. North Butyl exhibited an increase in the loss modulus between 50 and 75°C, the temperature range over which a discontinuity in the permeation as a function of reciprocal temperature was observed. The details are available in Ref. 5. The glass transition (T_g) temperature for each of the polymers was also determined. The T_g, Storage moduli, and tan δ are presented in Table 4. These data indicate that T_g for Butyl rubber is about -60°C; the other gloves have significantly higher T_gs at -30°C for polyurethane and approximately -16°C for Hypalon® and Viton®. The composite glove of polyurethane-Hypalon® has a T_g that is intermediate between polyurethane and Hypalon®, while Viton®-Hypalon® has a more complex T_g that exhibits a total of three transitions. The additional transition may be due to an interaction between the Viton® and Hypalon®. The glass transition temperatures for gloves with single transitions are presented graphically in Figure 7. All of the T_gs are well below room temperature, so no adverse effects are predicted for them during operations.

Table 4. Average measured Tg, Storage Modulus, and Tan δ for all the samples.

	~Approx T_g (°C)	Actual T_g (°C)	Storage Modulus at T_g (Mpa)	Tan δ at T_g
G15	-60.8	-68.6	4201	0.137
G30	-60.6	-68.7	4397	0.133
N15	-60.7	-68.4	3795	0.140
N30	-60.2	-68.1	4306	0.130
P15	-60.6	-68.4	2794	0.137
P30	-60.4	-68.7	4288	0.132
P15ESDB	-60.6	-68.4	3739	0.136
P24ESDB	-59.6	-69.4	3566	0.136
P25Y	-16.2	-25.1	1489	0.067
P15U	-30.6	-39.2	1852	0.068
P20UY	-24.1	-35.3	1935	0.055
J24V	-17.0	-24.5	2738	0.089
J31V	-16.5	-24.4	2749	0.100

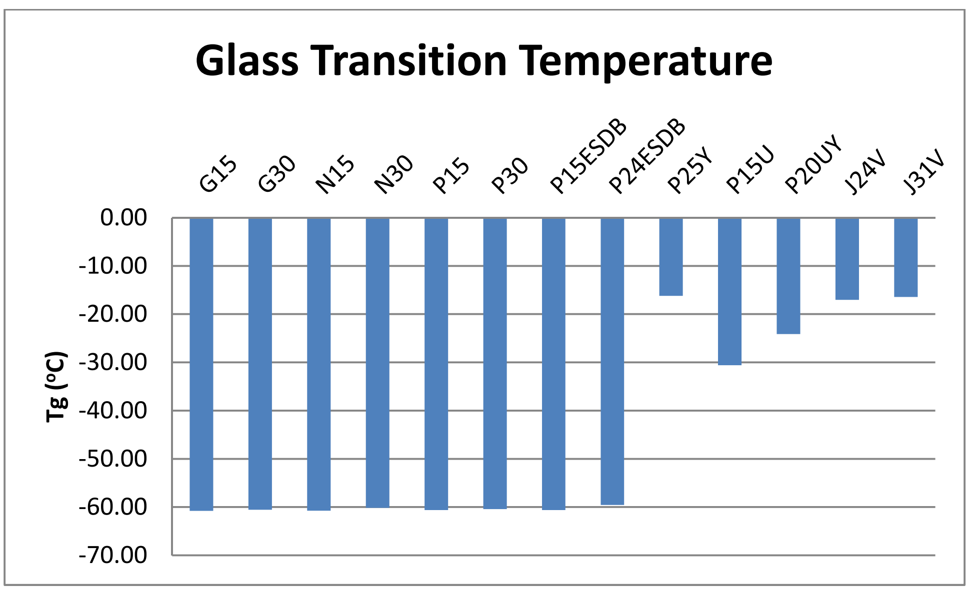

Figure 7. Glass transition temperatures for the gloves tested in this study that exhibited single T_g.

Summary and Conclusions

Butyl Rubber samples from gloves supplied have a permeability of between 5 and 11 barrers at room temperature.

The Viton® rubber gloves exhibit the lowest permeability for both air and hydrogen.

Thicker butyl gloves reduce the amount of tritium released from glove boxes.

All of the gloves exhibit some off-gassing of an unknown compound, and additional testing with appropriate analytical test apparatus is recommended.

All of the gloves meet or exceed the 100 lbf/in requirement stated in ASTM D120 for electrical gloves. The Butyl gloves exhibit puncture resistance in excess of 200 lbf/in and the Polyurethane gloves exhibit the highest puncture resistance with a value of nearly 750 lbf /in. Jung Butyl Viton® glove failed in a two stage manner with the lowest puncture resistance.

The Piercan Polyurethane gloves were the strongest material tested. They exhibited the highest tensile strength, well over minimum tensile elongation, and the highest load to failure. They were also one of the thinnest gloves tested which may offer improved tactile response.

The glass transition temperature, T_g, of the materials used in gloves of interest for SRS Tritium Facility glovebox use was determined. The T_g of all the butyl gloves was consistent and about -60°C. The composite gloves exhibited three different behaviors: the Polyurethane-Hypalon® had a T_g that was intermediate between Polyurethane and Hypalon®; the butyl-Viton® glove exhibited two distinct T_gs, at approximately the same values as the component constituents; while the butyl-Hypalon® composite material exhibited three distinct T_gs; one that was at approximately each of the constituent materials and a final one that was about 2°C.

All of the T_gs are well below room temperature and so brittle behavior is not expected for any of the glove materials in Tritium Facility operating conditions. Even the highest measured T_g, of 2°C for the Jung Butyl-Hypalon®, is well below room temperature.

The North butyl exhibits an increase in the loss modulus at temperatures between 50 and 75°C. The reason for this increase was not evaluated; however, the temperature range that this deviation was observed in is consistent with the observed change in the plot of log permeation rate as a function of reciprocal temperature.

Acknowledgements

The authors would like to thank Tritium Operations, Tritium Engineering, and Tritium Extraction Facility for technical and financial support. We would also like to acknowledge Med Allen for facilitating this study and acting as liaison between SRNL / SRS and the glove manufacturers.

References

1. SRNL-STI-2012-00028, Evaluation of Glovebox Gloves for Effective Permeation Control, P.S. Korinko, Y. Breakiron, Feb 29, 2012
2. SRNL-STI-2012-00030, Thermogravimetric Characterization of Glovebox Gloves, P.S. Korinko, Y. Breakiron, Feb 29, 2012
3. SRNL-STI-2012-00068, Puncture Test Characterization of Glovebox Gloves, P.S. Korinko, Y. Breakiron, G. K. Chapman, Feb 29, 2012
4. SRNL-STI-2012-00069, Characterization of Tensile Strength of Glovebox Gloves , P.S. Korinko, Y. Breakiron, G. K. Chapman, Feb 29, 2012
5. SRNL-STI-2012-00070, Dynamic Mechanical Analysis Characterization of Glovebox Gloves, P.S. Korinko, Y. Breakiron, Feb 29, 2012
6. ASTM D120-09, Standard Specification for Rubber Insulating Gloves, West Conshohocken, PA 19428, 2009.
7. ASTM D412-06, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension, West Conshohocken, PA 19428, 2006.