The Contribution of Rubber Adhesion to Sealability at Deep Freeze Temperatures

Cathy Zhao, PhD
West Pharmaceutical Services, Inc

2020 PDA Asia Pacific Aseptic Processing of Biopharmaceuticals Conference

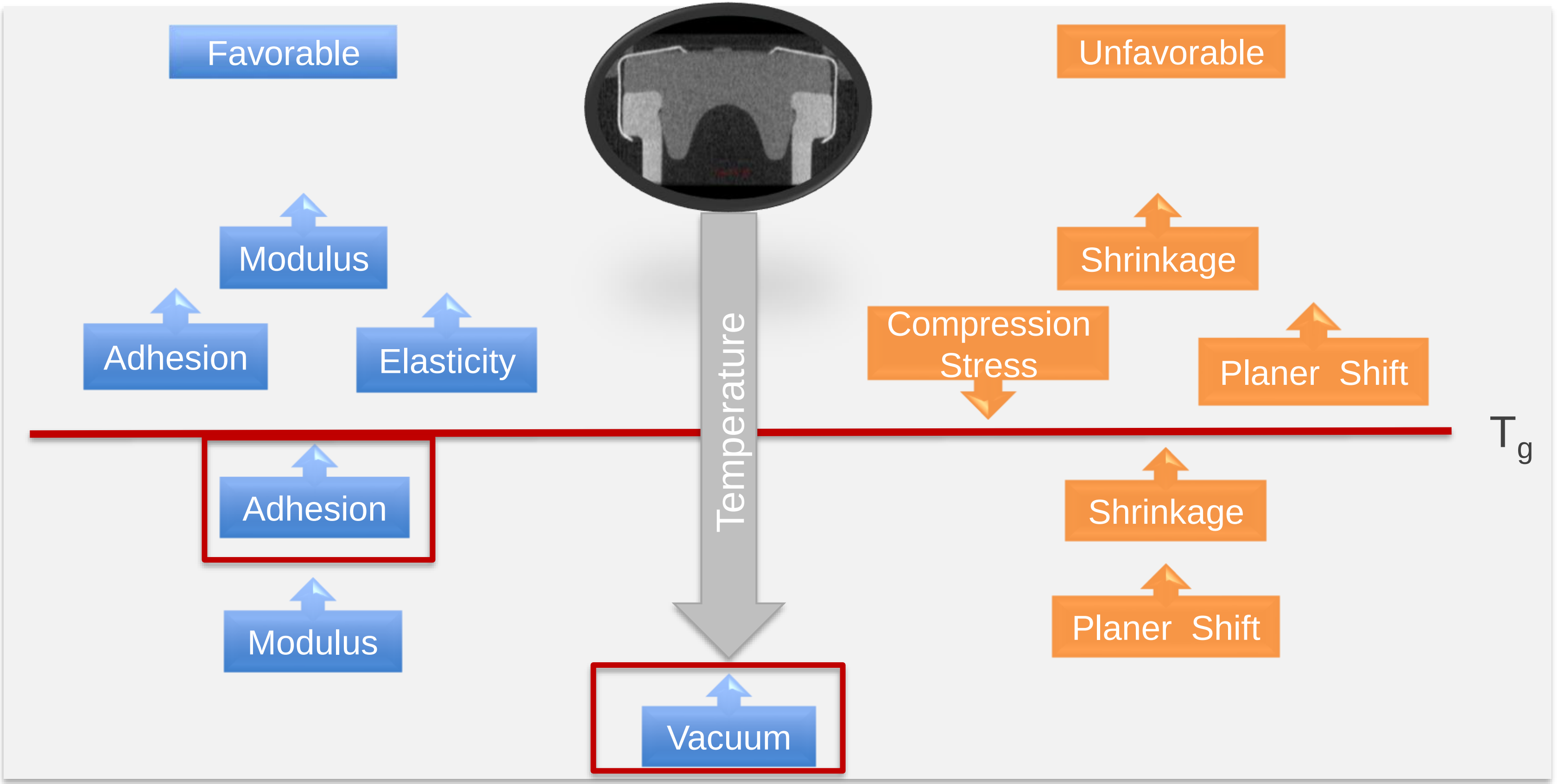
Agenda

Purpose

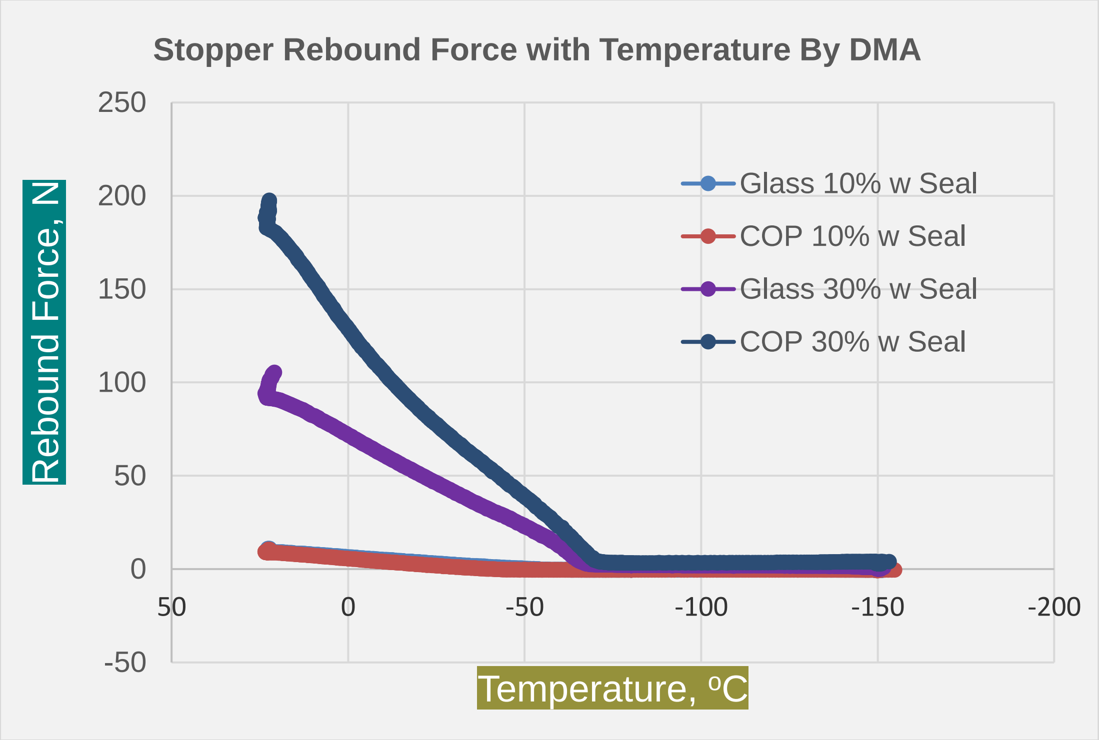
- Elasticity above & below T_g
- What makes rubber seal at temperatures below T_g?
- Shrinkage above & below T_g
- Does polymer chain co-mingling occur between rubber and COC/COP vials?
- The lower the T_g, the better sealability at low temperatures?

COC – cyclic co-polymer; COP – cyclic polymer.

Factors Impacting Vial Stopper Sealability



Rubber Stoppers Lose Elasticity Below T_g



DMA Testing conditions:
Compression: 10% & 30%
1) Isothermal for 1hr @ RT
2) Cool to -80ºC at 1ºC/min
3) Cool to -150ºC at 10ºC/min

DMA – Dynamic Mechanical Analysis

Shrinkage of Rubber above & below T_g

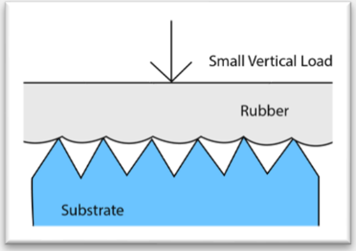
Coefficient of Linear Thermal Expansion (CLTE)

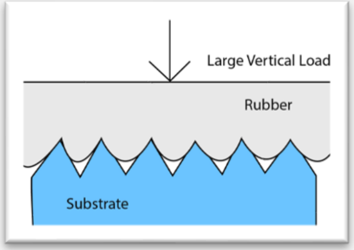
SAMPLE	T_g by DMA, °C	CLTE (/°C) x 10^{-6}, T_g – 125 °C	CLTE (/°C) x 10^{-6}, -120 °C - T_g
Rubber 1	-55	293.7	74.1
Rubber 2	-86	305.6	89.87
Rubber 3	-55	221.7	62.84
Rubber 4	-55	222.0	65.10

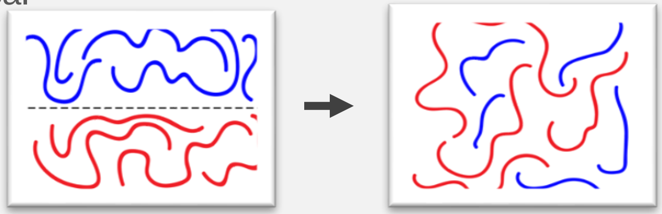
- Rubber shrinkage varies with formulations.
- The shrinkage is much higher above T_g than below T_g.
- T_g and CLTE do not have direct correlation.

General Adhesion Mechanisms[1]

- Physical adsorption – intermolecular interactions with intimate contact
  - Wettability
  - COC/COP vs glass with rubber
- Mechanical adhesion – interlocking surfaces by filling voids and pores of surfaces
  - Contact area: surface roughness, pressure, viscosity…
- Diffusion – merge at interface by diffusion
  - molecules mobile and soluble, oil in thermoplastic elastomer (TPE)
  - polymer chains ends inter-penetration at interface
  - contact time, temperature, molecular weight, physical forms…
- Chemical bonding
- Electrostatic







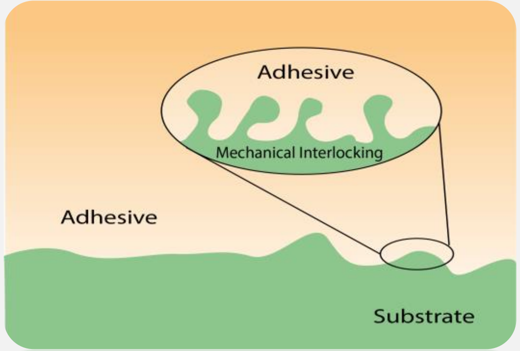
[1] Adapted from: S Athavale, Adhesion and Must be cited as: Adhesives Theory presentation, September 10, 2010, SIES College of Arts, Science & Commerce, Nerul, Navi Mumbai, India.

How Does A Rubber Seal Achieve Adhesion?

General Adhesive

Two steps to achieve adhesion:

- Wetting
- Solidification



Rubber Adhesion[2]

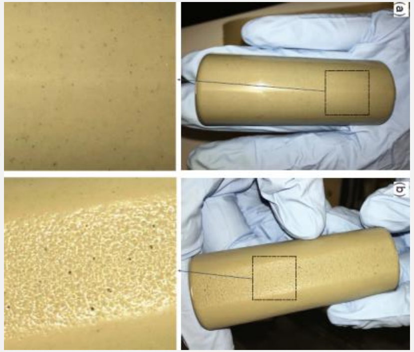
Two steps to achieve adhesion:

- Close contact under pressure
- Chain frozen at T_g

HNBR T_g- -16ºC

10-20% CS @ RT

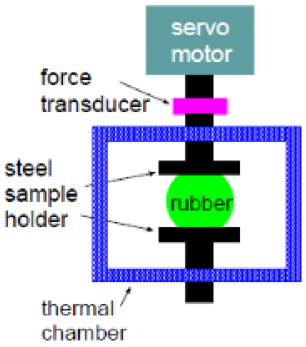
On PMMA
Cooled to -40ºC



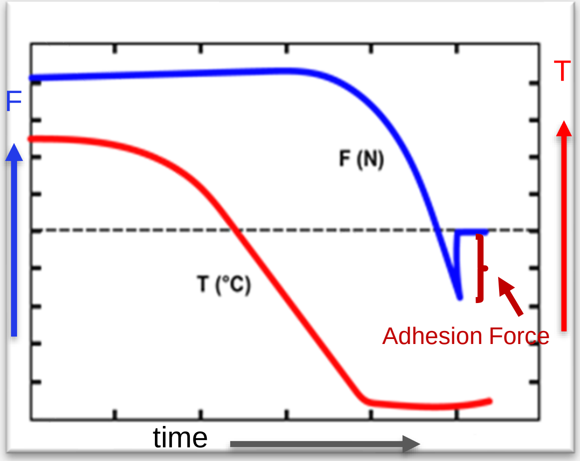
HNBR - Hydrogenated Nitrile Butadiene Rubber; CS – compression strain; RT – room temperature.

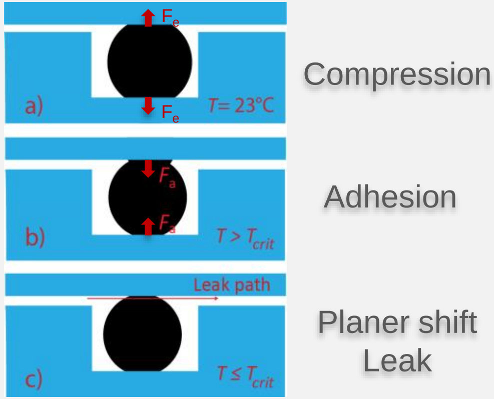
[2] AG Akulichev, A Tiwari, L Dorogin, AT Echtermeyer and BNJ Persson. Rubber adhesion below the glass transition temperature: Role of frozen-in elastic deformation. EPL, 120 3 (2017) 36002.

Role of Adhesion on Rubber Sealability Below T_g [2,3]



DMA - Initial compression strain 10% at RT, cooled down to -50°C.





Two different math equations of adhesion force: $T > T_g$ and $T < T_g$

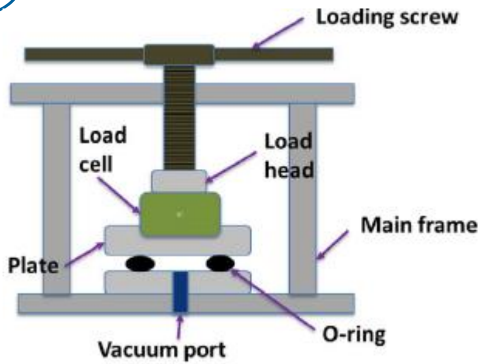
$T > T_g$: JKR (Johnson-Kendel-Roberts) Theory $f_C = -\frac{3\pi E_0^* a_c^2}{4R}$

$T < T_g$: $f_{\text{pull-off}} \approx (2\pi\omega a E_1^*)^{1/2}$

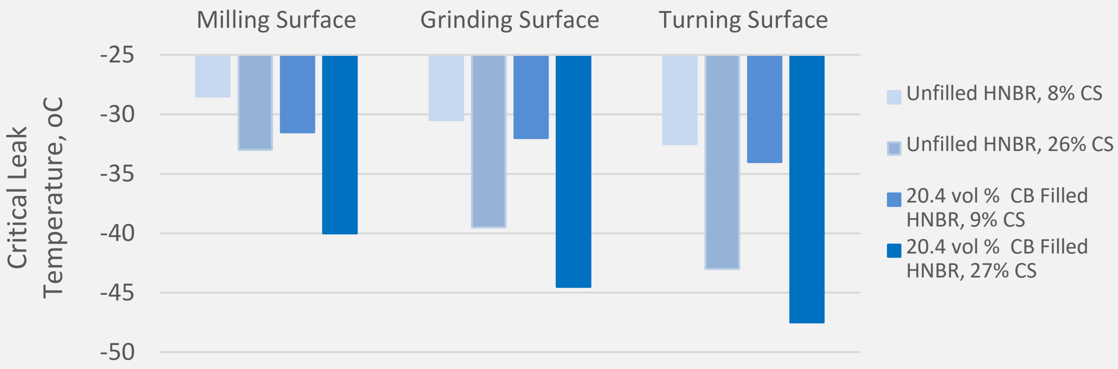
[2] Adapted data from: AG Akulichev, A Tiwari, L Dorogin, AT Echtermeyer and BNJ Persson. Rubber adhesion below the glass transition temperature: Role of frozen-in elastic deformation. EPL, 120 3 (2017) 36002.

[3] AG Akulicheva, AT Echtermeyer, BNJ Persson, Interfacial leakage of elastomer seals at low temperatures, International Journal of Pressure Vessels and Piping, 160 2018 (14-23).

Rubber Seal Leak Temperature Determination[3]



HNBR: non-filled and 20.4% CB filled
Compression: 7% & 30%
Sealing surface: milling, grinding & turning
T_g: ~-16°C (DMA), -23°C (DSC)
Vacuum: 100 kPa



Rubber seal leak temperature depends on adhesion force, which depends on:

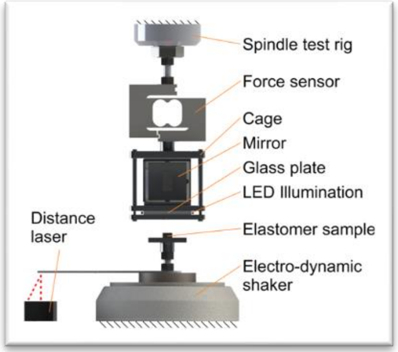
- rubber formulation
- sealing surface topography and
- compression

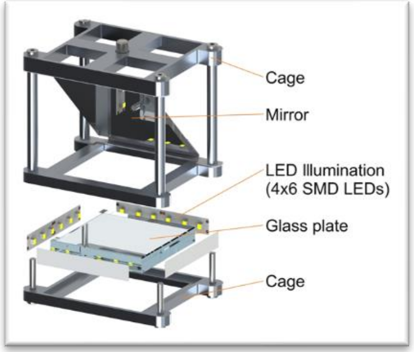
$$\Delta T_{\mathrm{adh}} = \frac{f_{\mathrm{adh}}}{2aE\alpha}$$

[3] Data and image adapted from: AG Akulicheva, AT Echtermeyer, BNJ Persson, Interfacial leakage of elastomer seals at low temperatures, International Journal of Pressure Vessels and Piping, 160 2018 (14-23).

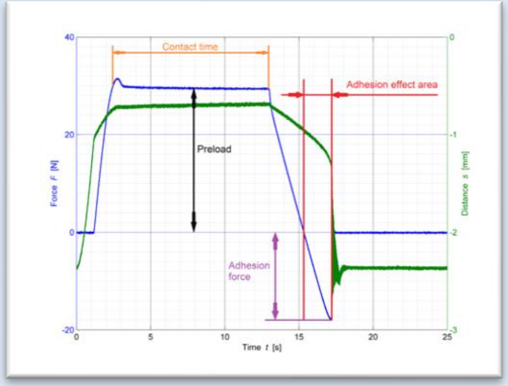
Adhesion Force Testing

Adhesion Test Rig





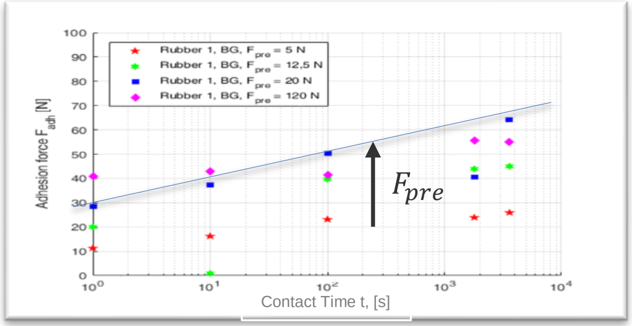
Adhesion Force & Visualization

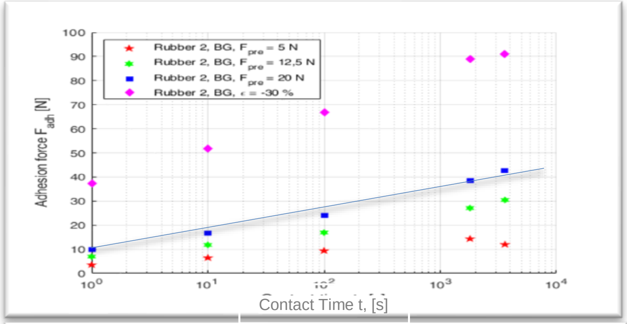


Rubber Adhesion At Room Temperature With COP & Glass

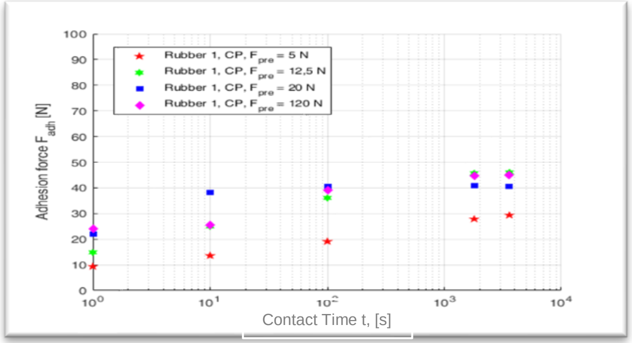
Rubber 1 | Rubber 2

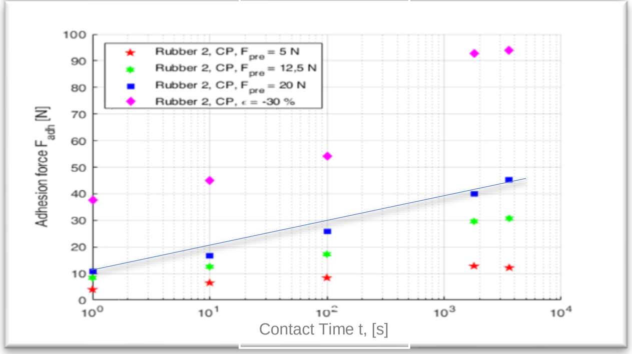
Glass





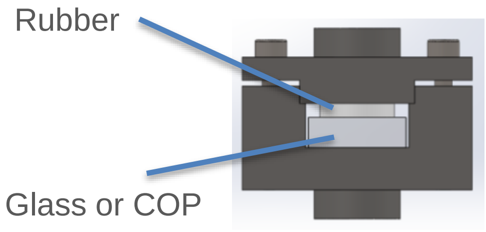
COP

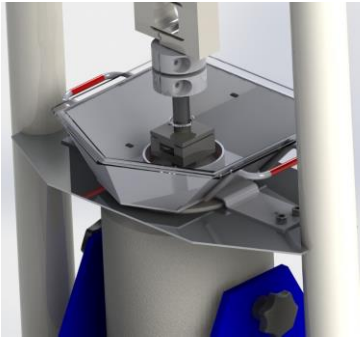


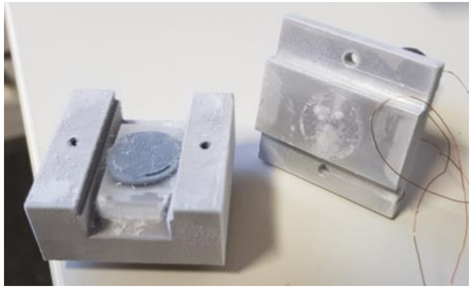


- Adhesion force is rubber formulation-dependent.

Deep Freeze Temperature Adhesion Testing Challenges





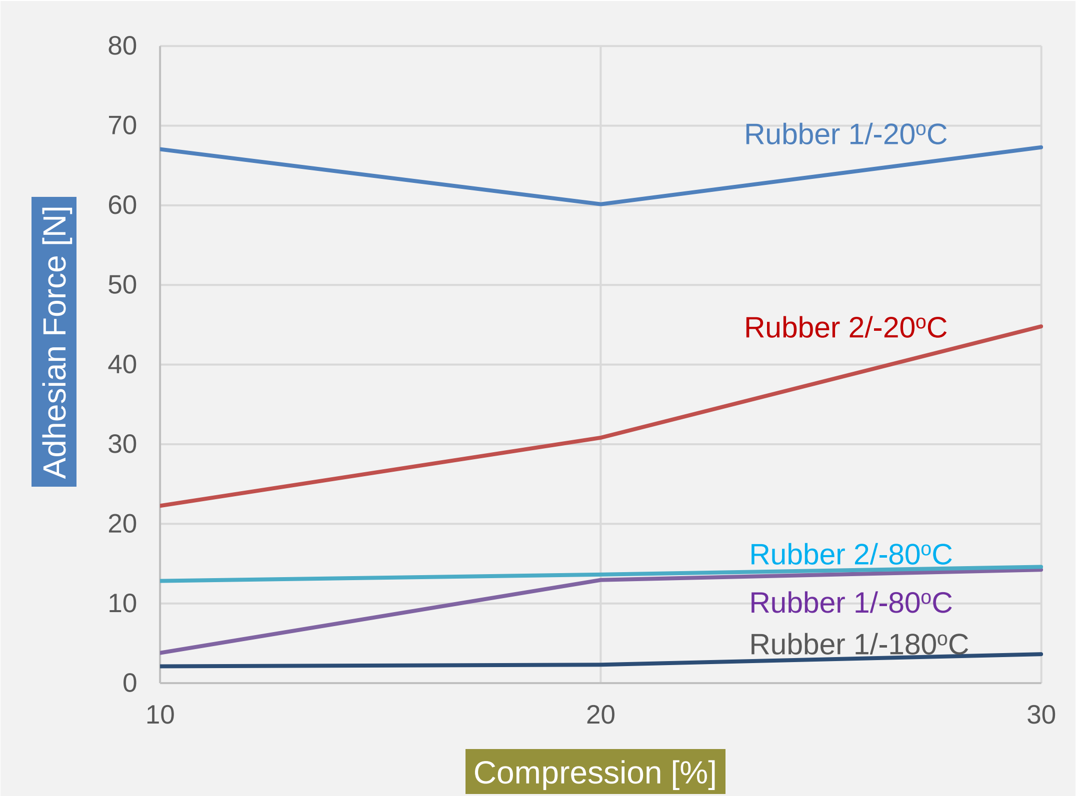


- Equipment limitation
- Time to equilibrium ≥ 4hours

- Ice generation
  - N_2 vapor
  - mold design

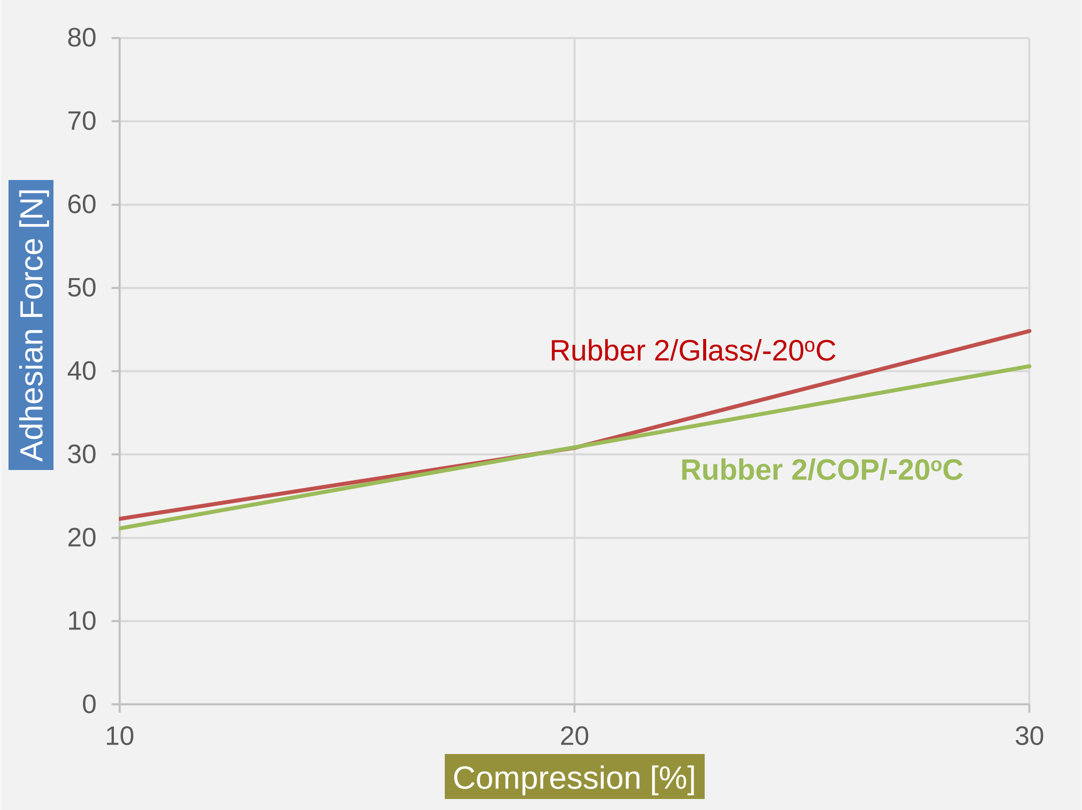
- Glue failure
  - steel & COP
  - steel & rubber

Rubber/Glass Adhesion at Low Temperature



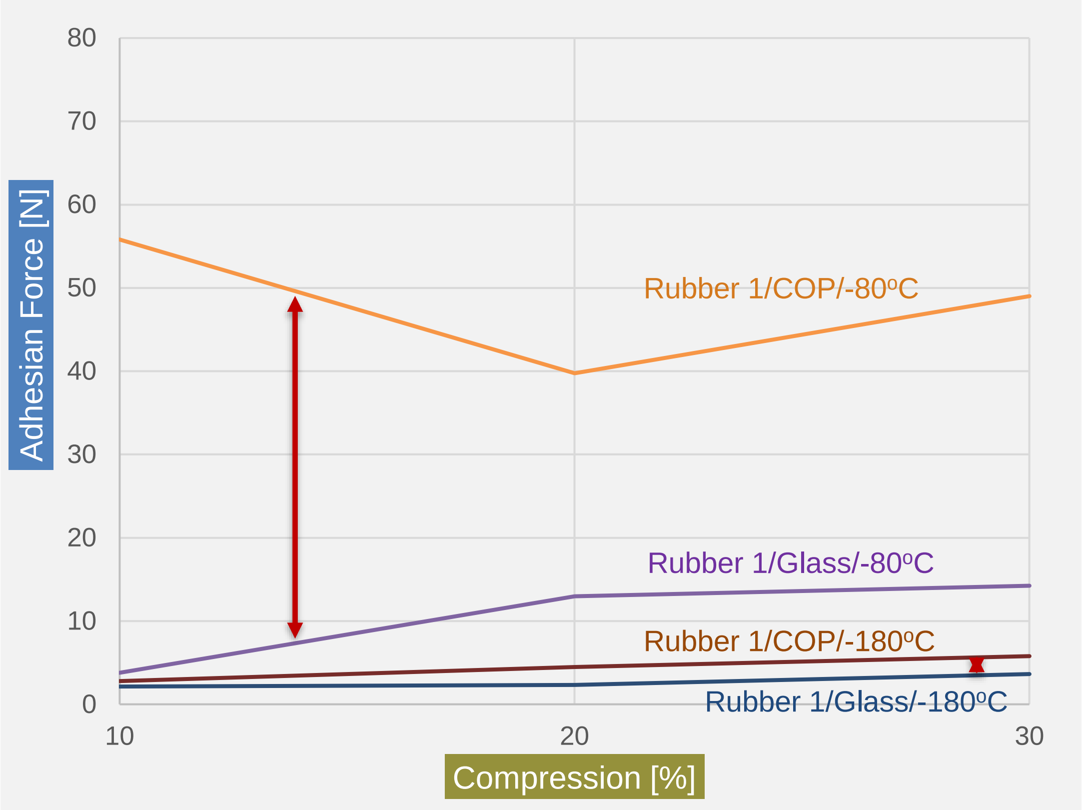
- Adhesion force to glass decreases with temperature for both rubbers.
- At 10% - 30% compression, no separation between rubber and glass occurred.

Rubber Adhesion to Glass vs COP at Low Temperature



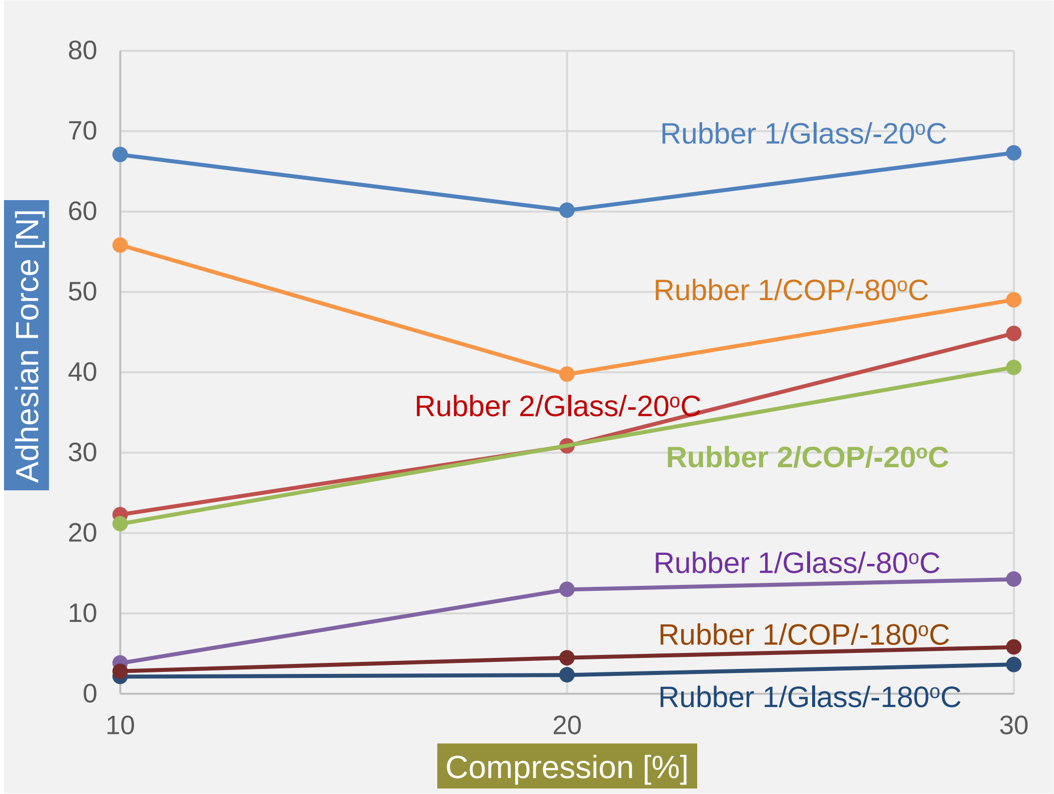
- The adhesion behavior of Rubber 2 at -20ºC is similar to room temperature.

Rubber Adhesion to Glass vs COP at Low Temperature



- Adhesion of Rubber 1 with COP is stronger than with glass at temperature below T_g.
- Rubber 1 generates additional adhesion with COP at temperature below T_g.

Rubber Adhesion to Glass vs COP at Low Temperature



- Adhesion of Rubber 1 with COP is stronger than with glass at temperature below T_g.
- Rubber 1 generates additional adhesion with COP at temperature below T_g.

Takeaways

1. Adhesion becomes the major sealing force at temperatures below T_g.
2. Mechanical adhesion generates at T_g, determined by rubber formulation, matrix material, surface roughness and compression pressure.
3. Rubber shrinkage is much higher at temperatures above T_g than below T_g.

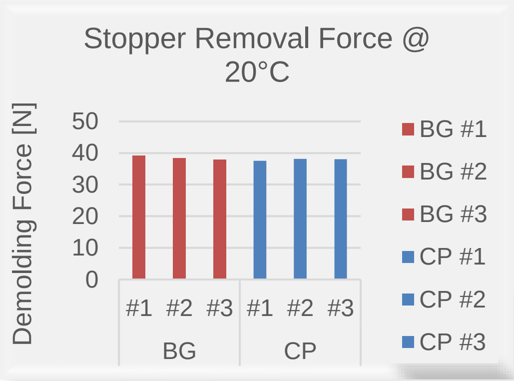
Future Work

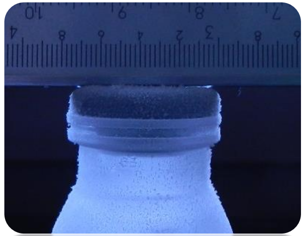
1 Test adhesion of CCS system at room temperature vs low temperature.

- Design
- Surface
- Lubrication
- Vacuum

2 Explore math modeling to predict leak temperature.

- Adhesion limit correlation with leak





CCS – Container Closure System

Acknowledgements

Professor Matthias Kröger, Freiberg University of Mining and Technology

Robert Teichert, M.Sc., Freiberg University of Mining and Technology

Le Ho, West Pharmaceutical Services, Inc

Fran DeGrazio, West Pharmaceutical Services, Inc

Allison Radwick, West Pharmaceutical Services, Inc

Thank You!