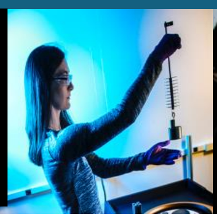
SAND2023-12493PE

Sandia National Laboratories

Metallic and Non-Metallic Material Compatibility in Super-Critical CO2 Environments



Roadmap for CO2 Transport Fundamental Research Workshop
Columbus, Ohio February 21 - 23, 2023

Topic 1C. Impact of impurities on non-metallic seals

PRESENTED BY

Bonnie Antoun, Nalini Menon

Sandia National Laboratories, Livermore CA

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Metal alloys compatibility in sCO_2 energy conversion systems

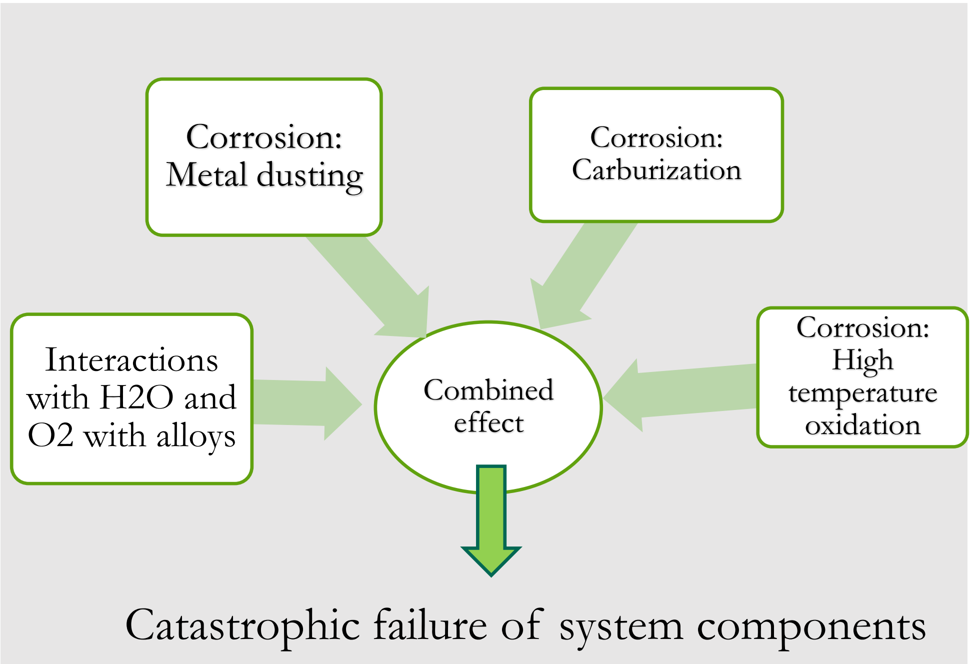
Environments + materials = Compatibility

Temperature	Component	Alloy	Type
T ≤ 250°C	Compressor, Gas cooler	304SS, P91, T22	Low cost austenitic or ferritic alloys
T ≤ 400°C	LT recuperator	347SS, 310SS, 316SS	Austenitic alloys recommended
T ≤ 550°C	HT recuperator, LT primary heater, LT Turbine	347SS, 310SS, 316L	Austenitic alloys with a lower level of Ni, Cr and Co (316)
T ≤ 650°C	HT Turbine, HT Primary Heater	Haynes 230, IN-617, 800H	Higher Ni/Cr alloys are recommended
T > 650°C	Very high temperature applications	Haynes 282, IN-713, IN-718 and IN-738, IN-690, IN-693, IN-725 and IN-740 and EP823	Little testing completed

Source: Review of supercritical carbon dioxide (sCO2) technologies for high-grade waste heat to power conversion
Matteo Marchionni1 · Giuseppe Bianchi1 · Savvas A. Tassou1
Received: 5 October 2019 / Accepted: 28 January 2020 / Published online: 11 March 2020

Metal compatibility in sCO_2 – Mechanisms of failure

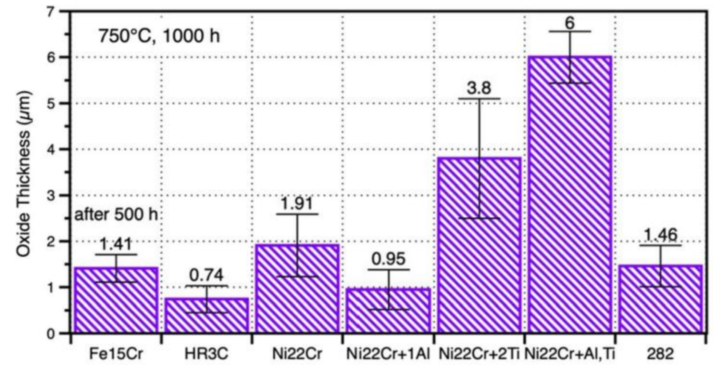
Mechanisms of degradation



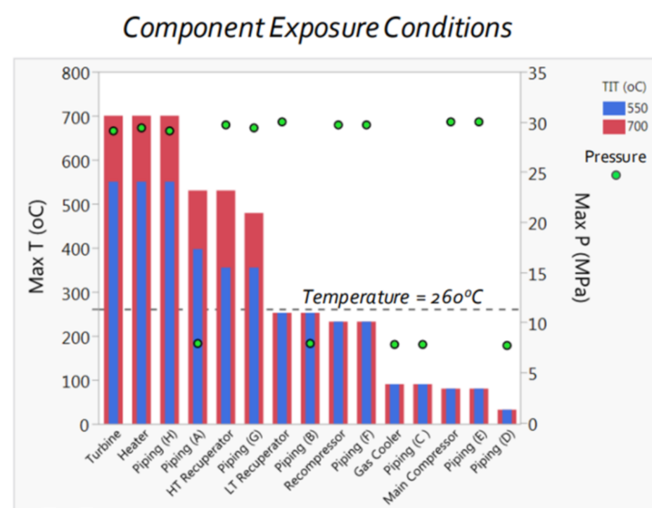
Mechanisms with impurities present

- Faster oxidation rates in Fe and Ni-based alloys
- Moisture increases the number of grain boundaries which act as diffusion routes leading to carburization beneath the scale

$$CO2(g) \rightarrow CO(g) + (1)\ 1/2\ O2(g)$$
$$2CO(g) \rightarrow CO2(g) + C(s)\ (2)$$



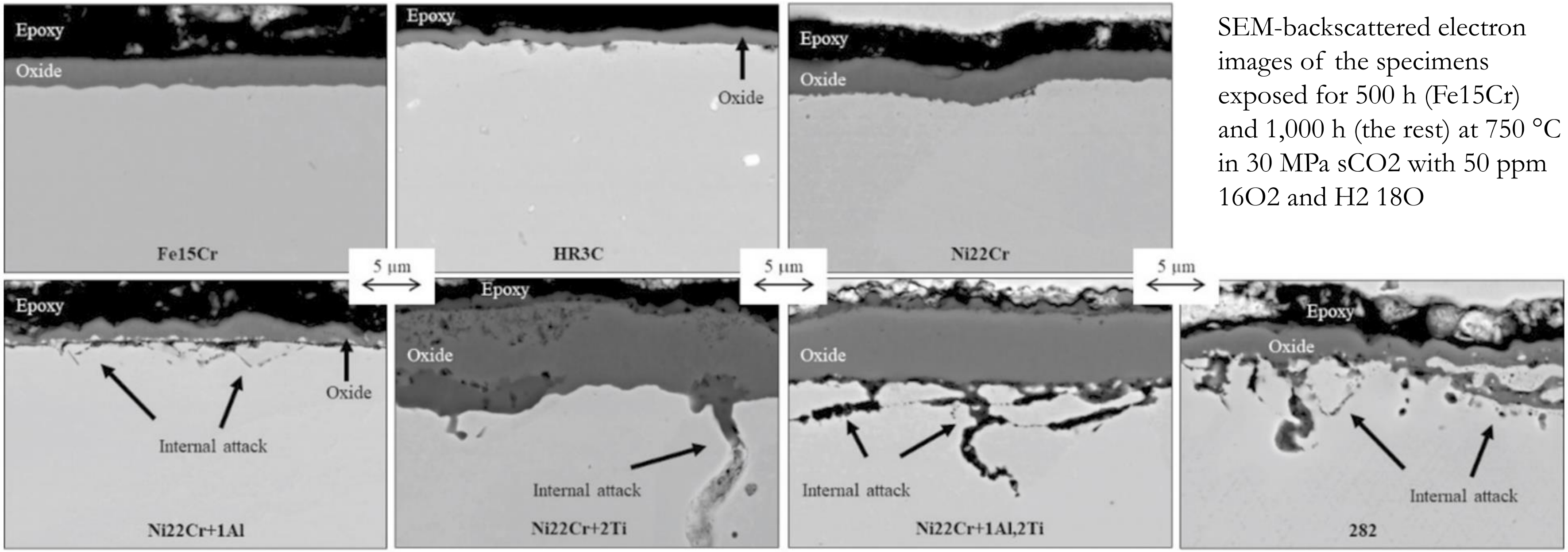
Measured oxide thicknesses after 1,000 h at 750 °C in 30 MPa sCO2 with 50 ppm 16O2 and H2 18O



Source: A Tracer Study on sCO2 Corrosion with Multiple Oxygen-Bearing Impurities Juho Lehmusto · Anton V. Ievlev · Ercan Cakmak · James R. Keiser · Bruce A. Pint; Oxidation of Metals (2021) 96:571–587

Source: Influence of CO2 Purity on the Corrosion of Structural Alloys for Supercritical CO2 Power Cycles; Matt Walker[1], E. Withey[2]; 6th International Supercritical CO2 Power Cycles Symposium, Pittsburgh, PA March 28th 201

Corrosion examples: Corrosion oxides on commercial and model alloys



SEM-backscattered electron images of the specimens exposed for 500 h (Fe15Cr) and 1,000 h (the rest) at 750 °C in 30 MPa sCO2 with 50 ppm 16O2 and H2 18O

Table 1 The chemical compositions of the alloys, measured by inductively coupled plasma and combustion analyses in weight%

Alloy	Fe	Ni	Cr	Al	Other
Fe15Cr	85.1	–	14.9	–	–
HR3C	51.0	20.4	25.7	–	1.2Mn, 0.5Nb, 0.4Si, 0.3Co
Ni22Cr	–	78.0	21.9	–	–
Ni22Cr + 1Al	–	76.2	22.8	1.0	–
Ni22Cr + 2Ti	–	76.2	21.8	–	2.0Ti
Ni22Cr + 1Al,2Ti	–	75.1	21.8	1.1	1.9Ti
282	0.2	57.1	19.6	1.6	6Co, 6Mo, 2.2Ti

Source: A Tracer Study on sCO2 Corrosion with Multiple Oxygen-Bearing Impurities Juho Lehmusto · Anton V. Ievlev · Ercan Cakmak · James R. Keiser · Bruce A. Pint; Oxidation of Metals (2021) 96:571–587

Polymer compatibility in sCO_2 energy conversion systems

Environments + materials = Compatibility

sCO_2 environments

Temperatures at 25-700°C
Pressures from 0.1 - 25 MPa
Cycling conditions
Pollutants (SOx and NOx)
Corrosive by-products
Presence of humidity

Materials
Polymeric materials for sCO2 environments

- FKMs, PTFE, FFKM
- Buna N, HNBR, Neoprene
- PEEK, PPS, HDPE, POM
- Nylon 6,6, PUR
- EPR, EPDM


Pressure transducers


Pressure relief valves


Valve seats


Turbo machinery seals

For turbines:
Inlet total pressure - 21 MPa (3045 psi)
Inlet total temperature - 753 K (480°C)
Mass flow rate – 1270.5 kg/s
Outlet static pressure – 7.35 MPa (1065 psi)

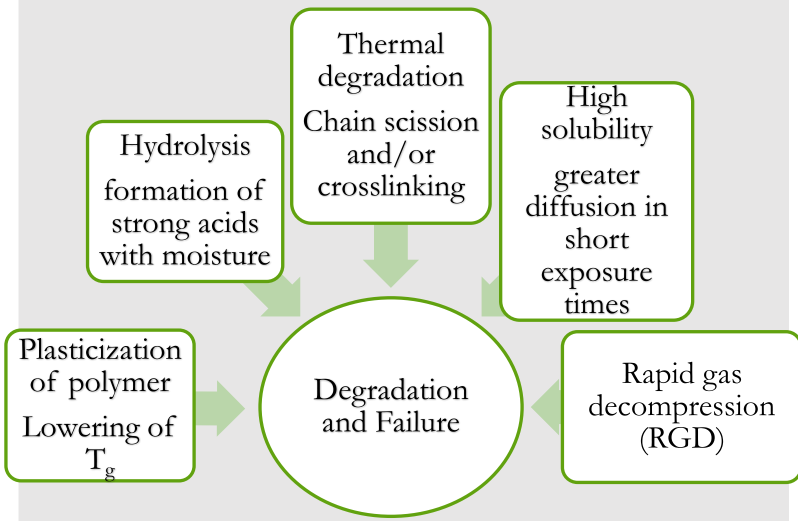
Gas type	Permeation coefficient (Q)	Diffusion coefficient (D)	Solubility coefficient (S)	S/D
N2	1	1	1	1
CO2	24	1	24	24
CH4	3.4	0.7	4.9	7
He	15	60	0.25	0.004
O2	3.8	1.7	2.2	1.29

Approximation of permeation, diffusion and solubility coefficients of various gases through common elastomers

High solubility and easy permeation through polymer

Polymer compatibility in sCO_2 – Mechanisms of failure

Mechanisms of polymer degradation



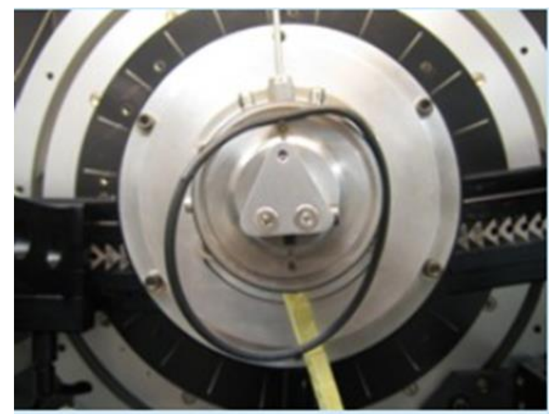
Influenced by

- High pressure (> 10 MPa)
- Higher CO_2 concentration in gas mixture
- Higher solubility of CO_2 in elastomer
- High decompression rate >0.1 MPa/min
- Elastomer microstructure
- O-rings with less design-imposed constraints

Amorphous or semi-crystalline polymer

Degree of crystallinity, substitution on backbone, molecular weight, crosslink density, glass transition temperature T_{g}, chain alignment/ packing

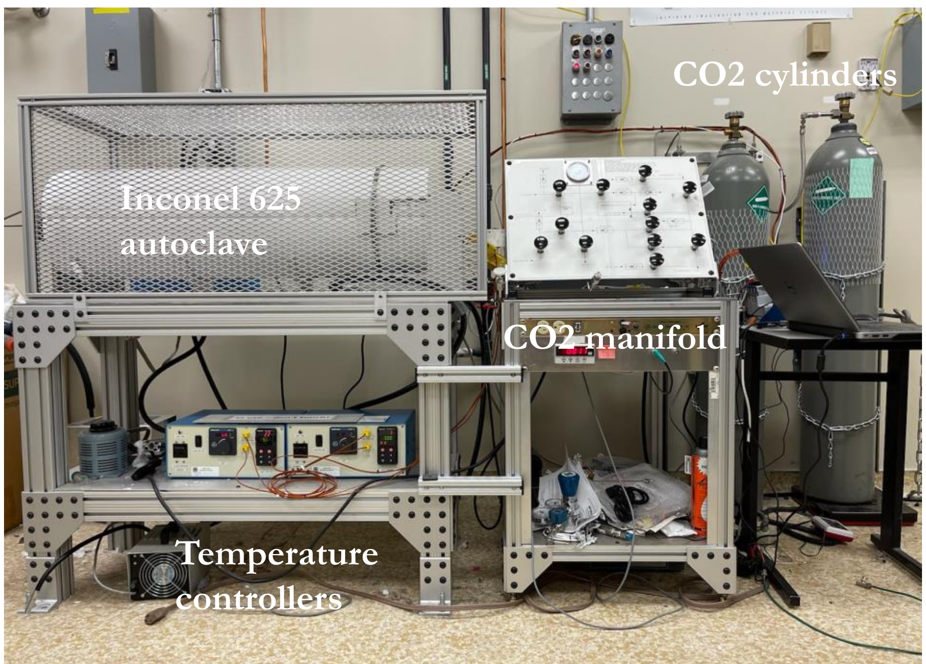
Examples of failures in elastomers in sCO2 service due to explosive decompression

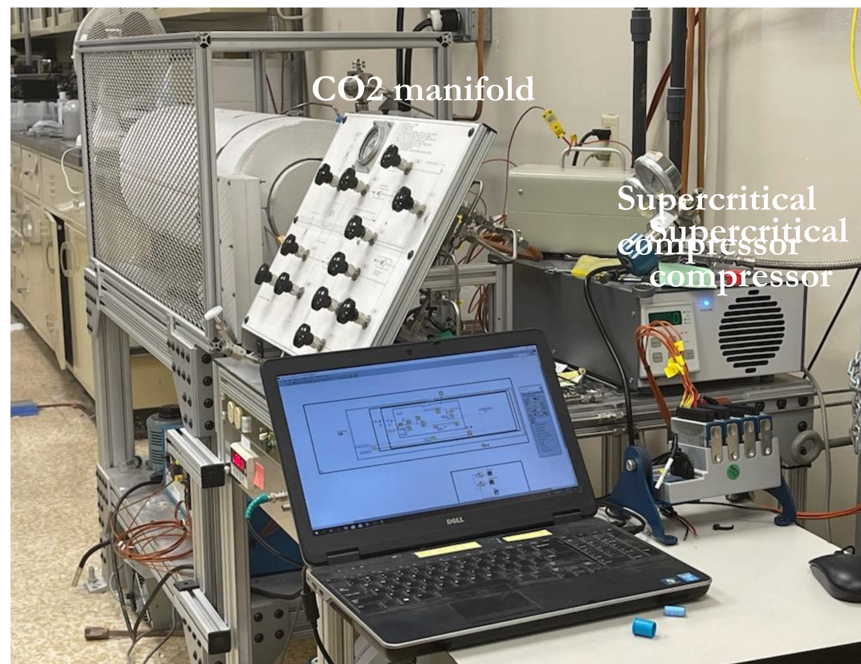


Failure seen with Viton O-ring due to sCO2 exposure

Sandia's sCO2 testing capability

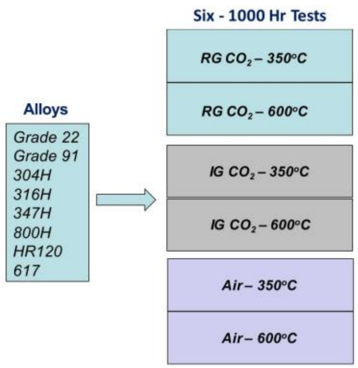
- Constructed in 2014 for testing of materials in the presence of liquid (supercritical) carbon dioxide (CO2) at high pressure (maximum operating pressure 3500 psi) and temperature (up to 650ºC); flow-through design
- System was modified in 2016 for corrosion studies with the removal of the CO2 compressor, enabling the use of gaseous CO2 at lower pressure (up to 300 psi) at 500C
- Research and development involving materials in sCO_2 up to 250°C for polymers and up to 650ºC for metal alloys
- Collaborative work and proposals for polymers and metal alloy work in Co2 and SCO2 invited



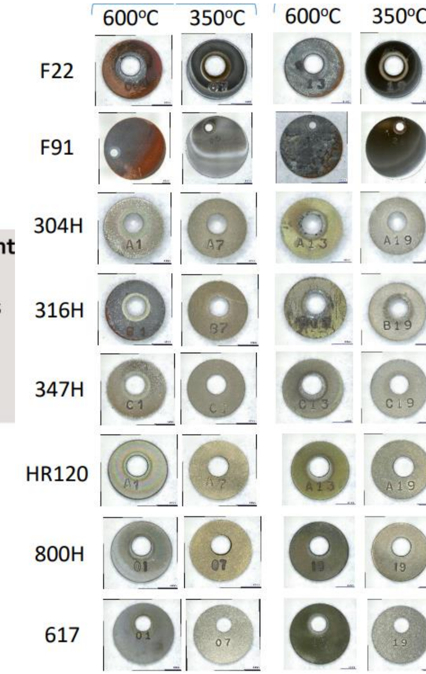


Metal alloy compatibility in sCO_2 – FY 2016-2018

Influence of CO2 purity on the corrosion of structural alloys for SCO2 power cycles



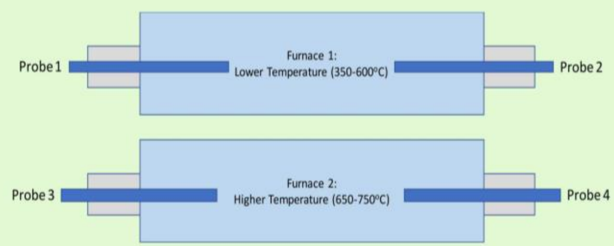
- **Post-Test Measurement**
  - ✓ Weight Change
  - ✓ Oxide Microstructures
  - Internal Carburization
  - Metal Loss – Lifetime Predictions



14. Digital microscope images of each alloy from the RG and IG CO_2 Experiments

Alloy	Chemical Analysis (Wt %)																			
	Fe	Cr	Ni	Mn	Co	Mo	Si	Al	B	C	Cu	P	S	Ti	W	Nb	N	V	Zr	Ta
F22	98.13	2..19	0.07	0.4	-	0.95	0.2	0.021	0.0001	0.1	0.1	0.008	0.011	0.002	-	0.001	-	0.004	-	-
F91	89.25	8.38	0.18	0.43	-	0.94	0.32	0.011	-	0.1	-	0.02	0.01	0.007	-	0.067	0.063	0.22	0.001	-
304H	70.54	18.16	8.08	1.39	0.32	0.4	0.44	-	-	0.049	0.51	0.032	0.0004	-	-	-	0.081	-	-	-
316H	68.60	16.61	10.26	1.536	0.152	2.006	0.329	-	-	0.041	0.392	0.036	0.001	-	-	0.005	0.0315	-	-	-
347H	68.73	17.24	9.32	1.83	0.45	0.38	0.66	-	-	0.06	0.51	0.028	0.019	-	-	0.74	0.017	-	-	0.02
800H	46.70	20.56	30.6	0.54	0.03	-	0.32	0.52	-	0.07	0.03	0.12	0.0001	0.57	-	-	0.01	-	-	-
HR120	35.48	24.91	37	0.68	0.15	0.27	0.5	0.08	0.002	0.062	0.09	0.012	<0.002	<0.01	<0.1	0.6	0.163	-	-	-
617	0.76	22.63	53.2	0.02	12.33	9.38	0.15	1.15	0.002	0.06	0.05	-	0.001	0.27	-	-	-	-	-	-

CO_2 Grade	Gas Chemical Analysis						
	CO_2 (%)	CO (ppm)	H_2 (ppm)	N_2 (ppm)	O_2 (ppm)	CH_4 (ppm)	H_2O (ppm)
RG	> 99.999	0.012	0.005	1.070	**0.040**	0.153	**< 0.02**
IG	> 99.980	< 0.010	0.040	35.370	**11.110**	0.430	**0.53**



- Run probes of 2 different alloys in two separate temperature ranges in CO_2
- Long duration tests up to 1500 hours
- Witness coupons (3) of each alloy included for extraction at 500 hour intervals (500hrs, 1000hrs, and 1500hrs)
- Lower T Candidates: 9Cr-1Mo (grade 91), 316, 304, 310, 347H
- Higher T Candidates: 800H, HR120, 617, 625, 230, 740H

Statistical Analysis Summary of Alloy Weight Change Differences for RG and IG CO_2

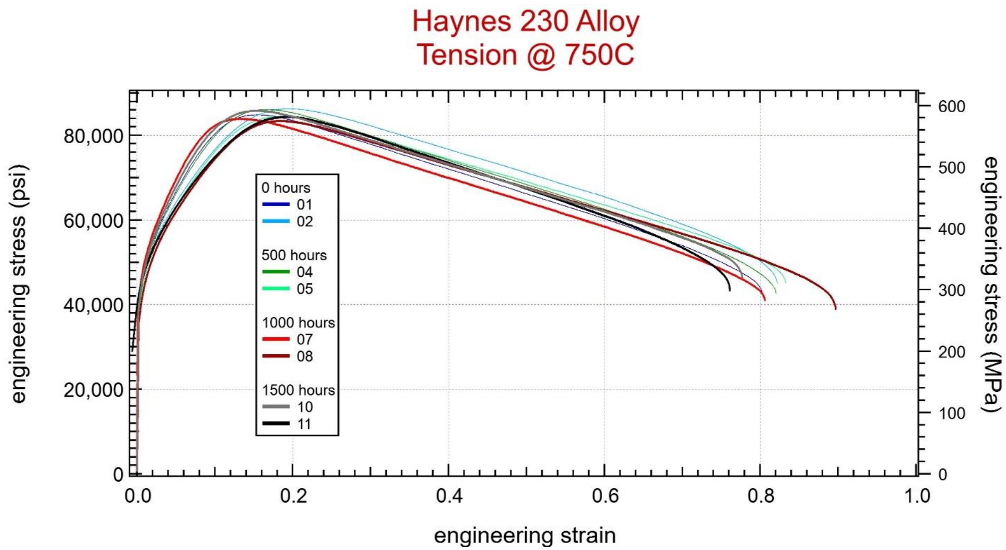
	350°C		600°C	
Alloy	500 hrs	1000 hrs	500 hrs	1000 hrs
F22	IG = RG	IG = RG	IG = RG	IG = RG
F91	IG = RG	IG = RG	IG = RG	IG = RG
304H	IG = RG	IG = RG	IG = RG	IG = RG
316H	IG > RG	IG > RG	IG = RG	IG = RG
347H	IG = RG	IG = RG	RG > IG	IG = RG
800H	IG = RG	IG = RG	IG = RG	IG = RG
HR120	IG = RG	IG = RG	IG = RG	IG = RG
617	IG = RG	IG = RG	IG = RG	RG > IG

Gas chemistry (RG vs IG CO2) has very little influence on alloy corrosion

Metal alloy compatibility in sCO_2 – FY 2019-2020

Effect of High Temperature CO_2 on Haynes 230 and 800H Alloy

- High temperature CO_2 on Haynes 230 and 800H alloys was investigated by subjecting the alloy samples to CO_2 at 650ºC for 500, 1000, and 1500 hours.
- Atmosphere was maintained with a constant flow of CO_2 from a gas cylinder at 150-200 mL/min
- After CO_2 exposure, the tensile specimen samples were tested in tension at 750ºC to failure
- For the eight tensile tests, data was collected at 1000 Hz for the following signals: displacement, 50-kip load cell, 10-kip load cell, extensometer, top thermocouple, and bottom thermocouple



Polymer compatibility in sCO_2 – FY2019-21

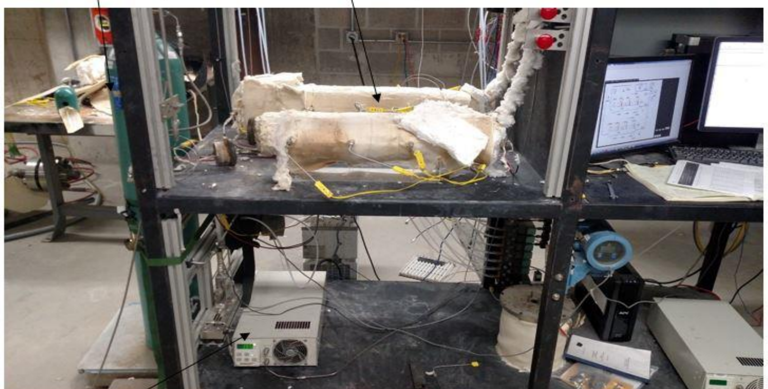
- Thermal behaviors of typical polymers at 100°C and 150°C temperatures at 20 MPa sCO_2 pressure in a 1000-hour exposure
- Pressure behavior of typical polymers at 10 and 40 MPa sCO_2 pressures at 100°C temperature in a 1000-hour exposure
- Behavior of soft polymers in the compressed state mimicking O-rings in sealing applications in sCO2 in a 1000-hour exposure
- O-rings with a barrier coat tested for diffusion mitigation of sCO_2
- Investigating the effect of thermal cycling (50°-150°-50°C) under steady 20 MPa sCO_2 pressure for 50 and 100 cycles

Sandia's CO2 and sCO_2 testing capability

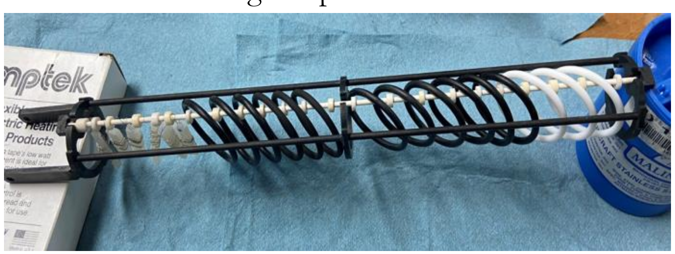
- In-situ monitoring of polymer degradation and failure modes
- Test methods and standards development
- Cycling experiments with sCO_2 pressure and thermal changes
- Solubility and permeation of sCO_2 in polymers and influence of fillers and plasticizers on this phenomenon
- Factors controlling rapid gas decompression – depressurization rates
- Effect of impurities such as H_2S and chemical aging of polymers

Polymer compatibility in sCO_2 – Sandia experiments FY2019-21

sCO2 test equipment and accessories



O-ring sample holder for autoclave



O-ring compression jig used in sCO_2 exposure; 25% deflection shim used

Ex-situ characterization for sCO2 effects*

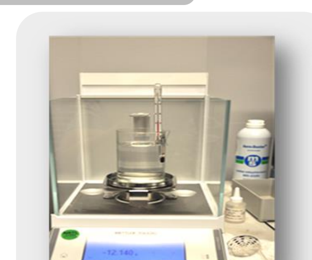
Elastomers (FKM, Buna N, HNBR, Neoprene, FF-202, EPDM, EPR)

- DMTA for T_g and Modulus
- Specific volume/density changes
- Compression Set
- ATR-FTIR spectroscopy

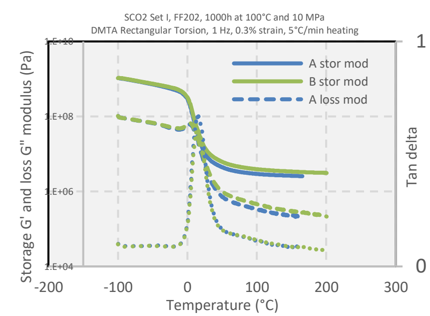
Thermoplastics (HDPE,PTFE, Nylon, PEEK, POM)

- DMTA for T_g and Modulus
- Specific volume/density changes
- Tensile Testing
- ATR-FTIR spectroscopy

Compression set test



Density measurements set-up



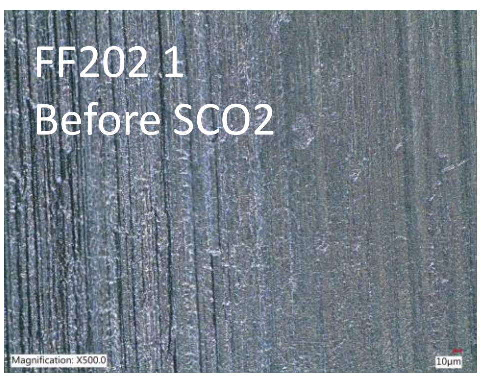
Samples were introduced as whole O-rings to test
Periodic removal of O-rings at 200 hours, 600 hours and at 1000 hours followed by cutting them to characterization test specimen dimensions

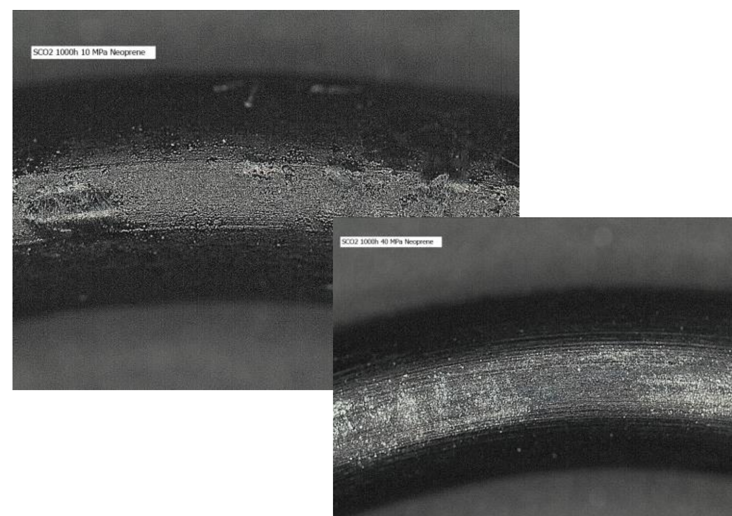
* = micro-CT and nanoindentation was used selectively

Results and Discussion – Major takeaways

Based on experiments on 13 polymers including both elastomers and thermoplastics and under conditions of testing shared, the following are high level findings:

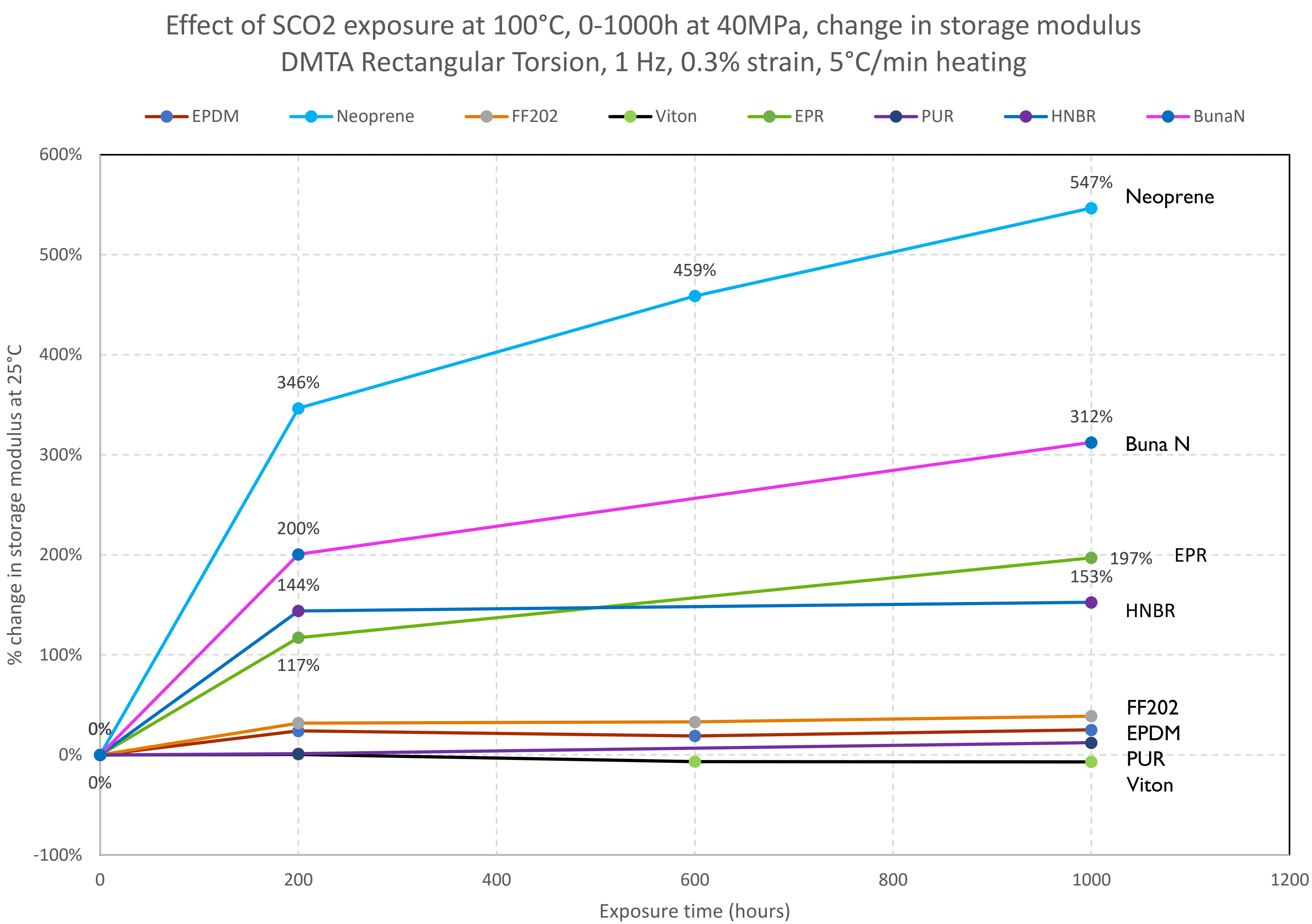
- **Thermoplastics showed minimal damage from sCO2 exposures compared to elastomers**
- **Elastomer showed internal cracks, surface texturization, structural changes, compression set changes**
- **Increasing temperatures accelerate damage mechanisms for almost all elastomers**
- **Increasing pressures in combination with long times of exposure accelerated damage in even robust polymers**
- **Increasing number of temperature cycles showed varying levels of damage in polymers**
- **Physical effects seen in the form of cracks inside the polymer and surface texturization**
- **Chemical effects seen in the form of changes in glass transition temperatures, storage modulus and structural changes in FTIR**



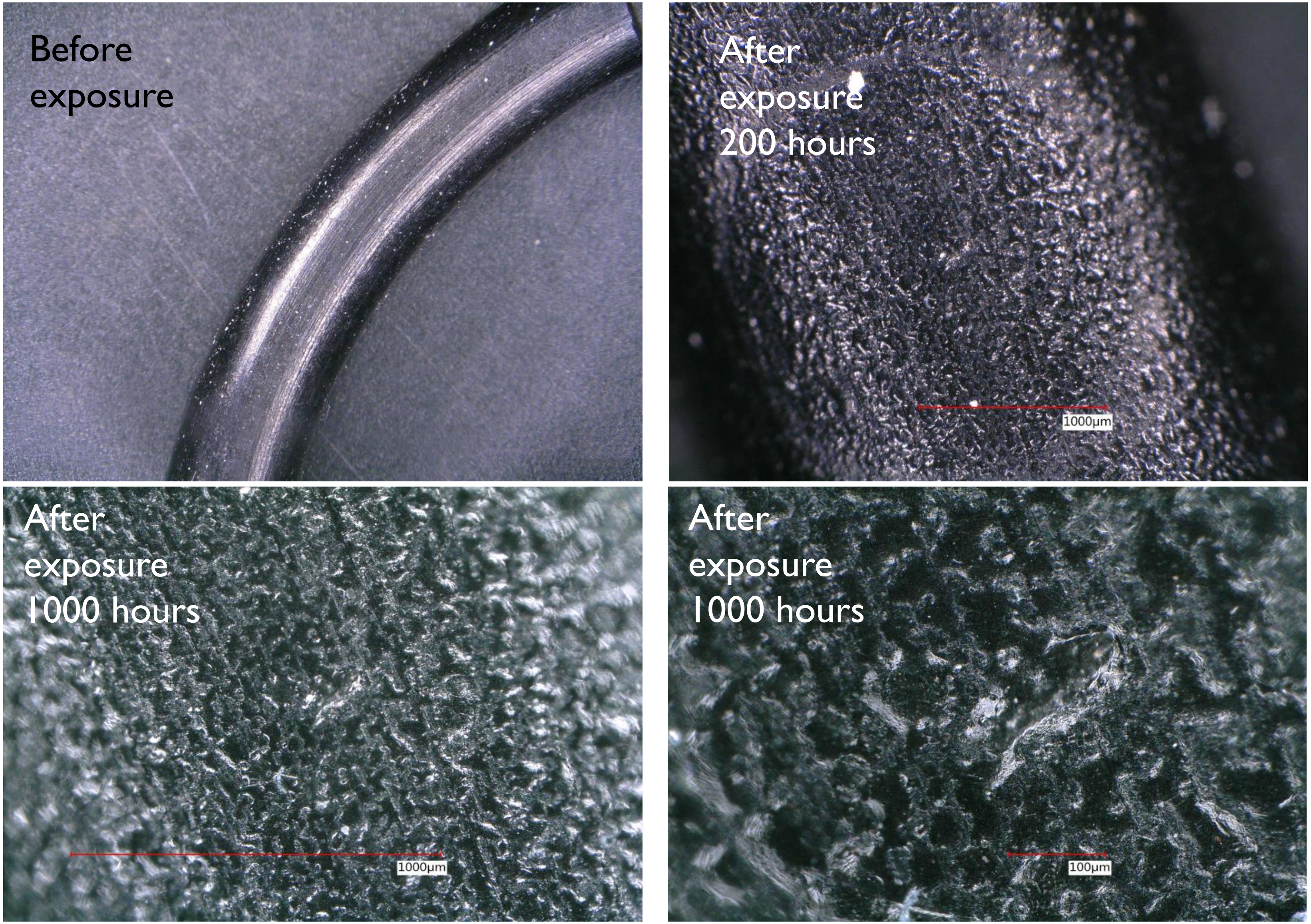


Dynamic Mechanical Thermal Analysis (DMTA) on different elastomers

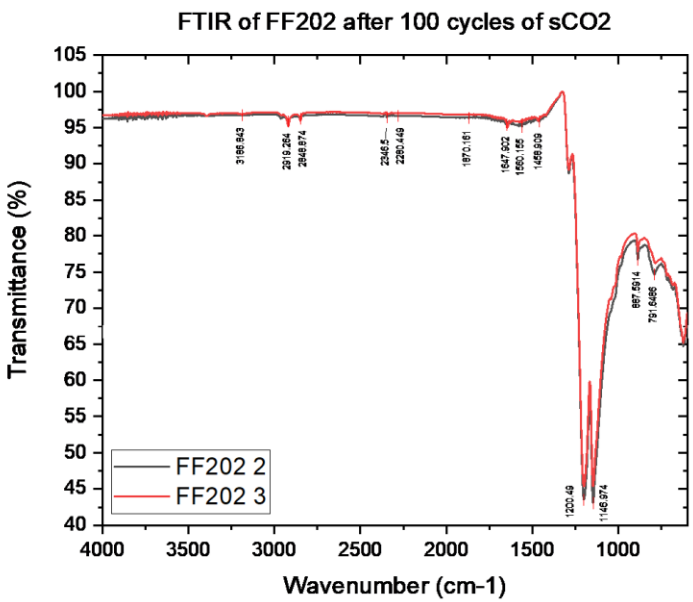
Exposure to 40 MPa sCO_2 at 100°C temperature

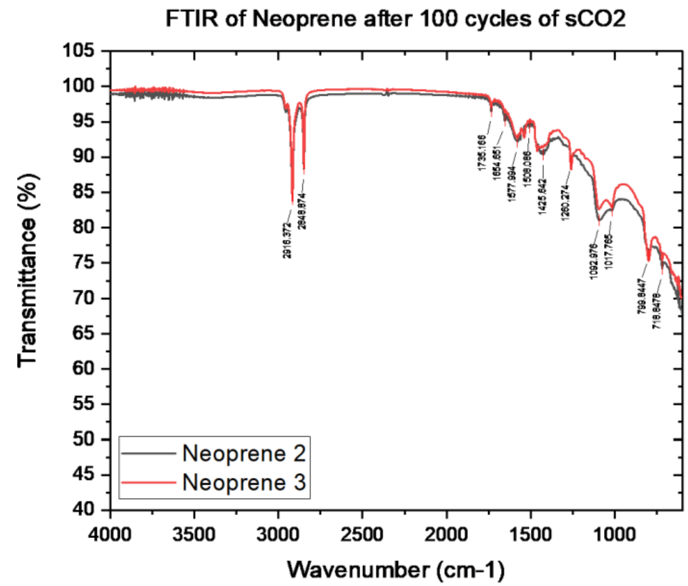


Optical microscopy images on Neoprene
100°C exposure @ 20 MPa sCO_2 pressure

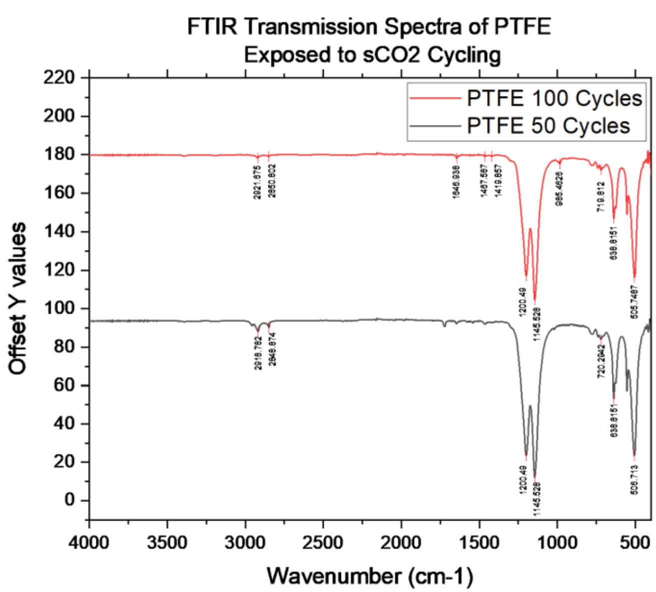


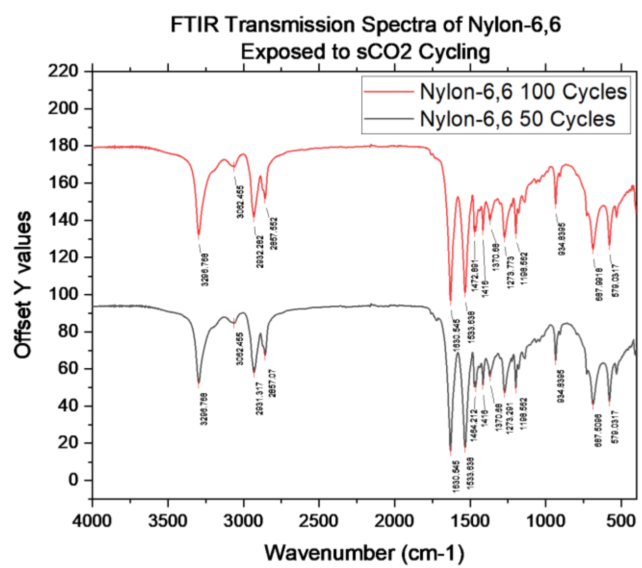
Attenuated Total Reflectance FTIR on polymers





Isothermal, isobaric sCO_2 exposure: 20 MPa pressure @ 100°C temperature

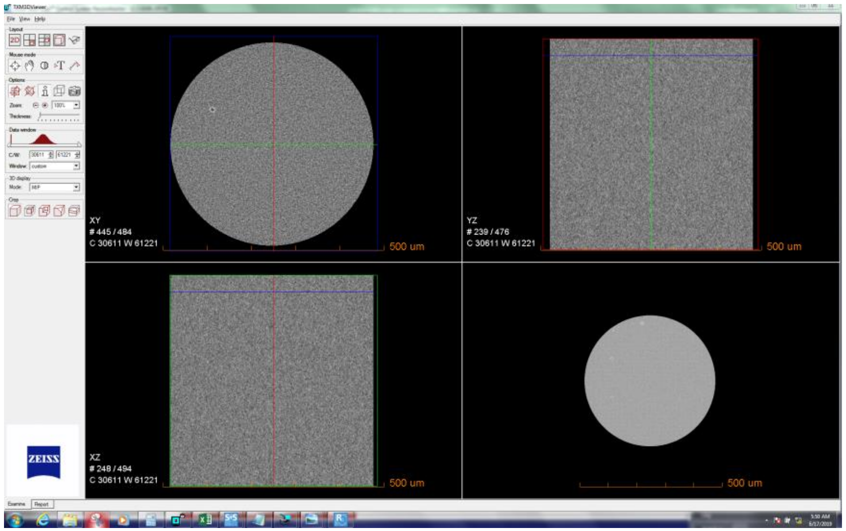




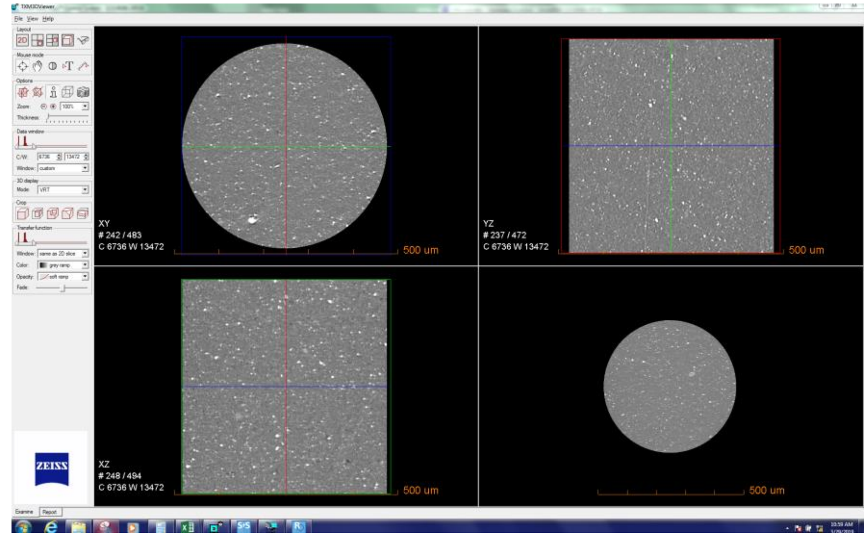
Isobaric Cycling temperatures sCO_2 exposure: 20 MPa pressure for 50-150-50°C thermal cycling

Micro-Computed tomography images for FFKM FF202 and EPDM rubbers
150°C exposure @ 20 MPa sCO_2 pressure

Unexposed

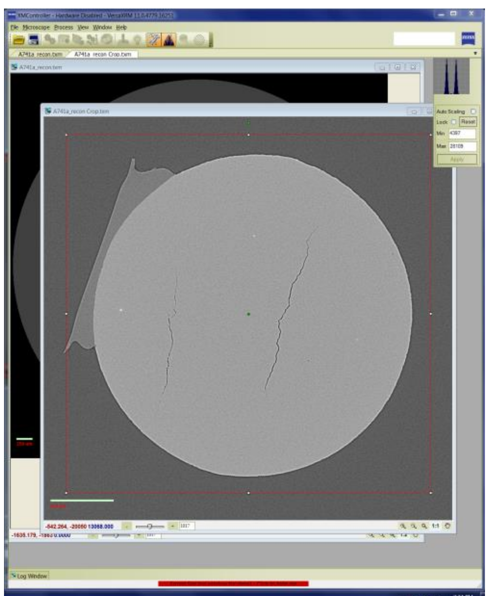


Unexposed



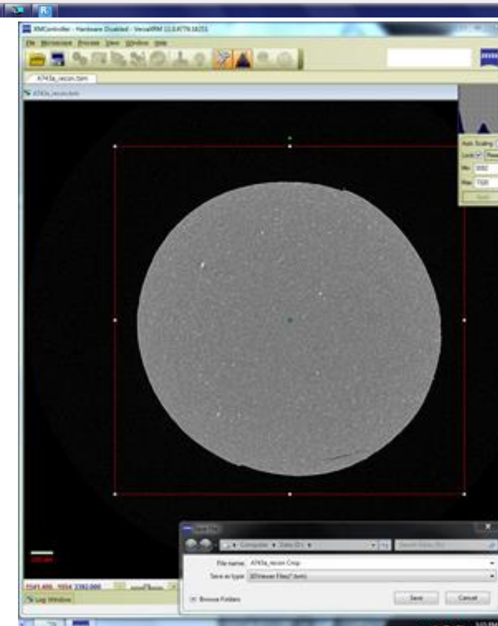
Exposed

500-1000 microns length cracks in the interior



Exposed

400-475 microns length cracks in the interior

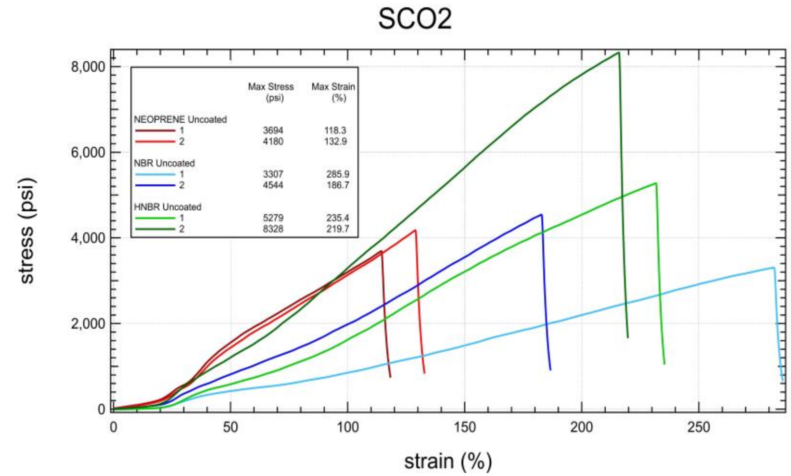


In both polymers cracks appear as early as after 200 hours of exposure at 100°C

Polymers held in compression fixture during test (25% deflection)

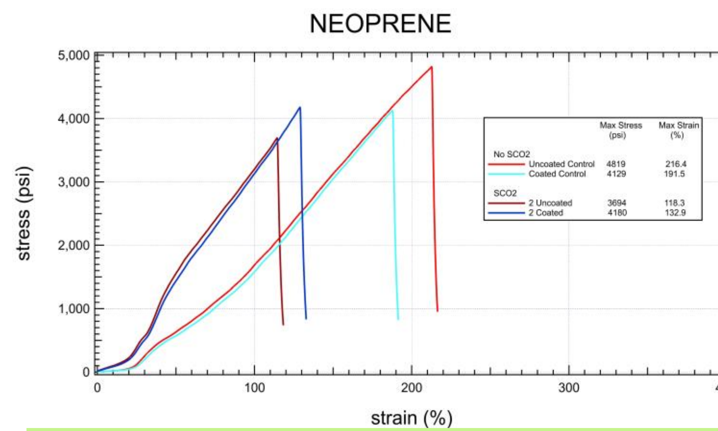
20 MPa sCO_2 pressure at 100°C

Compression fixtures designed to hold the O-rings inside the sCO2 autoclave



Elastomer-sCO_2 effects impact mechanical properties

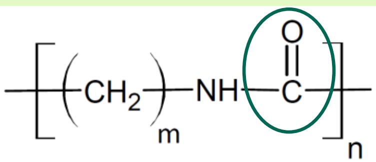
Picture of whole O-rings after compressed exposure to 20 MPa sCO2 at 100°C: from left – top row: Viton sample 1, Buna N, EPDM, HNBR; bottom row – Viton sample 2, EPR, Neoprene (uncoated) and Neoprene (coated)



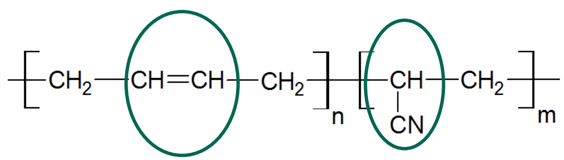
SCO_2-exposed Neoprene fails at lower % strain over unexposed

Results and Discussion – Major takeaways

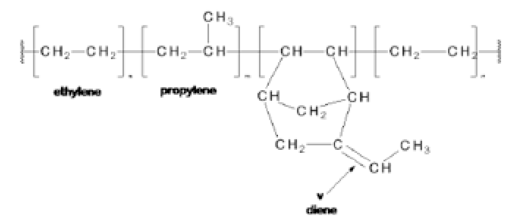
- Polymer backbone and microstructural details showed a great influence on behavior in sCO_2 environments
  - Presence of polar functionality -C=O, -C-Cl, -C-CN or -C=C- (double bonds) on backbone in polymers tested increase propensity for sCO_2 effects – for e.g. higher storage modulus with/without increase in T_g
  - Large pendant-group atoms (such as fluorine) can provide steric hinderance and decrease sCO_2 diffusion – for e.g. FF-202, FKM and PTFE
  - EPDM and EPR show property changes but less propensity to accelerated sCO_2 attack
  - Hard to separate influential factors in a given polymer type due to lack of information on the COTS materials used
    - influence of molecular weight, degree of crystallinity , crosslink density, fillers and additives, choice of polymer base with custom polymers (supplier-to-supplier differences)



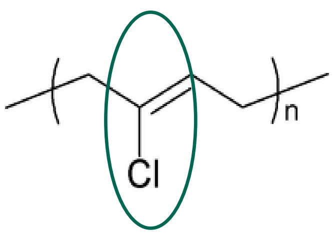
Polyamide (Nylon)



Nitrile butadiene rubber (NBR)

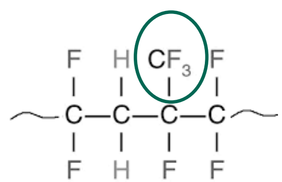


Ethylene propylene diene Monomer (EPDM)

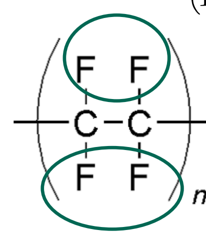


Polychloroprene (Neoprene)

FKM

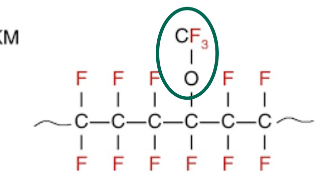


Fluoroelastomers (FKMs)



Polytetrafluoroethylene (PTFE)

FFKM



Perfluoroelastomers (FFKMs)

Impact of Sandia materials compatibility work

- **Multiple proposals, publications and presentations at conferences**
- **Collaborations with industry (material selection and testing) and University partnerships**
  - **For polymers - ExxonMobil - invited presentation Feb 2022 (POC: Garrett Wu)**
  - **For polymers - University of Wisconsin Madison (2018 onwards)**
- **International Supercritical Carbondioxide Symposium participation**

Next Steps – Recommendations (not currently funded)

- Impact of CO2 impurity level on non-metallic materials and seals
  - New and emerging materials
  - Coatings research for various seal materials
- Effect of CO2 impurities on metallic material
  - For transport applications
  - Fracture toughness testing during active CO2 exposure (with and w/o impurities)
  - Testing under realistic, in-service environments, including service/maintenance activities
  - Testing welds and connections – not just base (pipeline) materials
    - Connections are always important
  - Testing flow-meters and devices that are in-line
    - Verify correct operation during long-term CO2 and impurity exposure

Thank you for your attention !!