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Polymer compatibility in super-critical CO_2 environments – behaviors in low temperature and pressure exposures

Presentation to the
7th International Super-critical Carbondioxide Power Cycles Symposium
Feb 21-24 2022

PRESENTED BY

Nalini Menon[1], April Nissen[1], Robert Horton[1] Fitzjames Ryan[1], Mark Anderson[2] Mohamed Elbakhshwan[2], Nathan Colgan[2]

[1] = Sandia National Laboratories

[2] = University of Wisconsin

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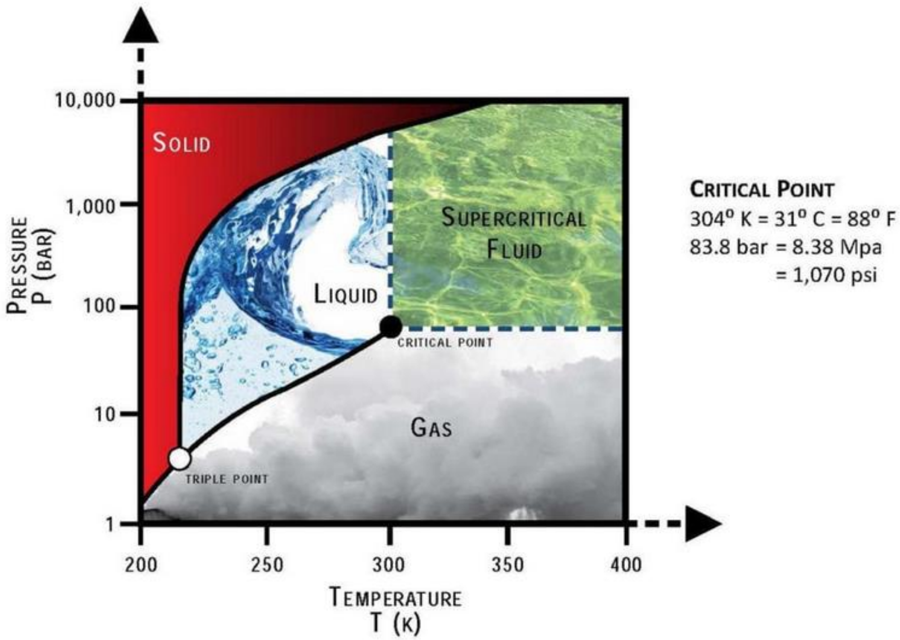
This work was supported by the Department of Energy (DOE) Supercritical Transformational Electrical Power (STEP) program FY2019-21

PRESENTATION TO EXXONMOBIL UPSTREAM RESEARCH COMPANY

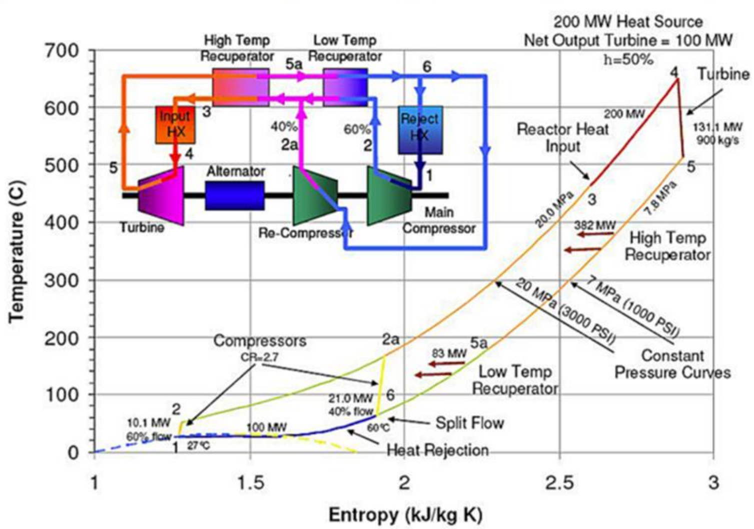
Content

- Why sCO_2 for power generation systems?
- Polymers in sCO_2 power generation
  - Typical service conditions and challenges
  - Current knowledge gaps
- Compatibility of polymers in sCO_2 environments
  - Current work
- Important takeaways from current work
- Future needs

Supercritical CO_2 for power generation



Supercritical CO_2 Brayton Cycle



- Easily achievable low supercritical pressures and temperatures
- Ideal working fluid – nonexplosive, non-flammable, non-toxic and relatively cheap
- High density and volumetric capacity compared to steam
- Smaller components, smaller plant footprint and lower capital costs
- Applicable to many thermal energy sources: fossil fuel combustion, nuclear, solar, geothermal, waste heat recovery
- **Carbon capture and utilization opportunity**

STEP's focus : better materials, designs, components, operation and control systems for commercial acceptance of large scale sCO2 power cycles

Highly recuperated closed loop Brayton test assembly, Sandia NM

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

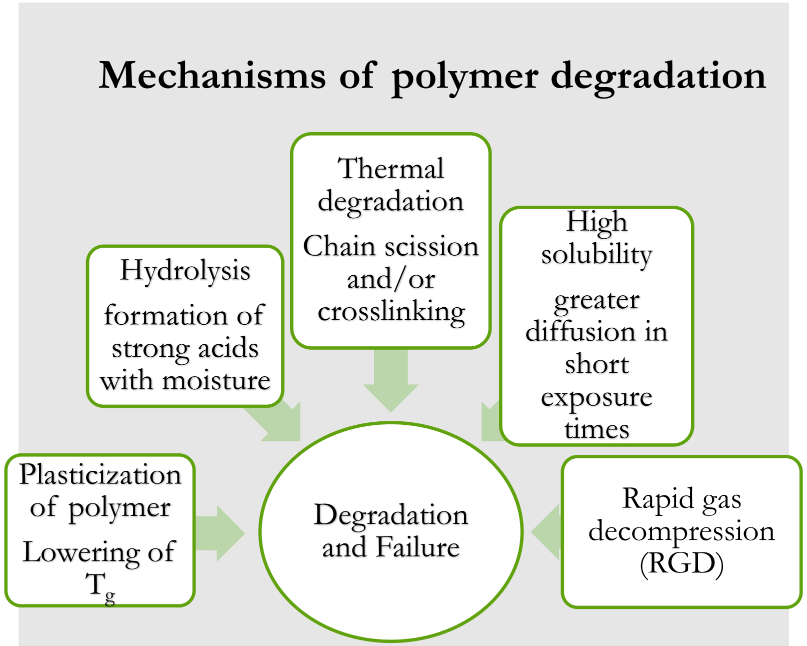
For turbines:
Inlet total pressure - 21 MPa (3045 psi)
Inlet total temperature - 753 K (480°C)
Mass flow rate – 1270.5 kg/s
Outlet static pressure – 7.35 MPa (1065 psi)

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

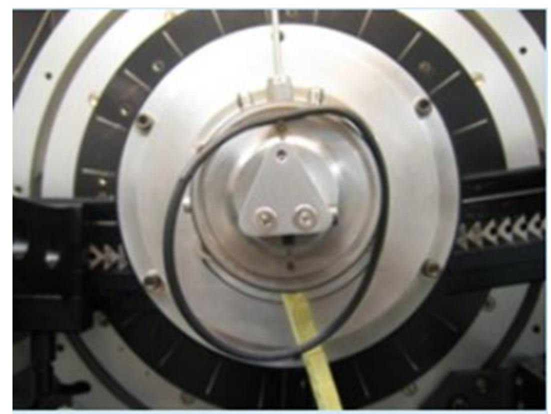


Increased by high pressure (> 10 MPa)
Higher CO_2 concentration in gas mixture
Higher solubility of CO_2 in elastomer
High decompression rate >0.1 MPa/min
Elastomer microstructure
O-rings with low degree of design-imposed constraint

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

Polymer compatibility in sCO_2 – Knowledge gaps

- Data for lower temperature (55-60ºC) and pressure (100-1800 psig) exists; R&D required for temperature range (60-150ºC) and pressures (4000-6000 psig)
- In-situ monitoring of polymer degradation and failure modes
  - polymer failure initiation and growth during the process instead of a post-mortem approach
  - physical and mechanical property degradation studies supported by chemical characterization
- Test methods and standards development
- Cycling experiments with changes in temperature and sCO_2 pressures
- 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
- Research and development for new material resistant to sCO_2 attack

Polymer compatibility in sCO_2 – Sandia experiments FY2019-21

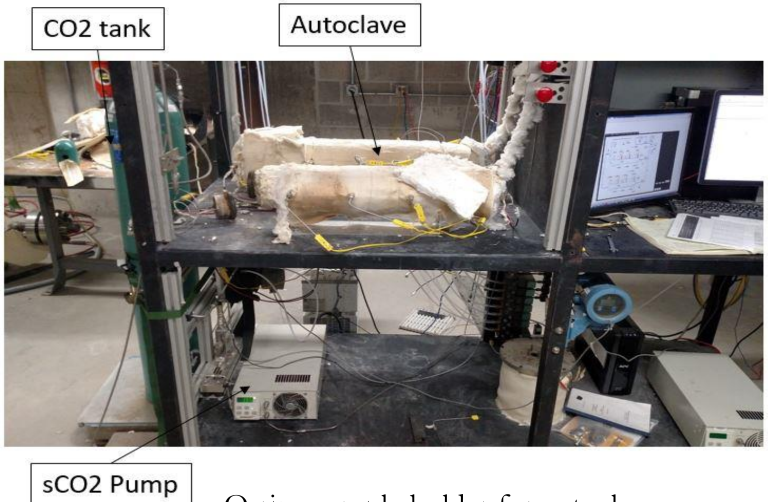
Sandia's sCO2 experimental work focused on establishing

- **baseline thermal behaviors of typical polymers at 100°C and 150°C temperatures at 20 MPa sCO_2 pressure in a 1000-hour exposure**
- **baseline behaviors of typical polymers at 10 and 40 MPa sCO_2 pressures at 100°C temperature in a 1000-hour exposure**
- **behavior of select polymers in the compressed state mimicking O-rings in sealing applications in sCO2 in a 1000-hour exposure; some O-rings with a barrier coat were tested for 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**

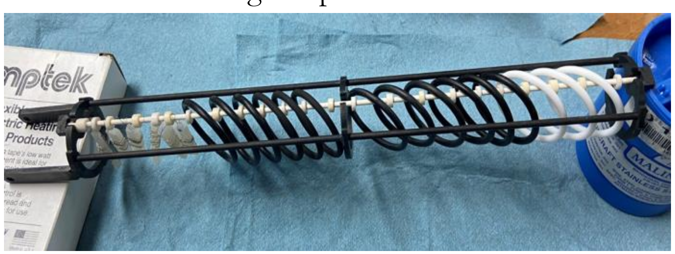
- **Addresses some of the critical knowledge gaps mentioned**
- **All experiments were possible due to collaboration with University of Wisconsin-Madison**
- **Sandia's sCO_2 test capability in place by end of FY 2021**

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*

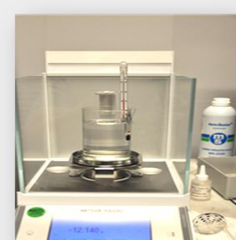
Elastomers (FKM, Buna N, HNBR, Neoprene, FF-202, EPDM, EPR)

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

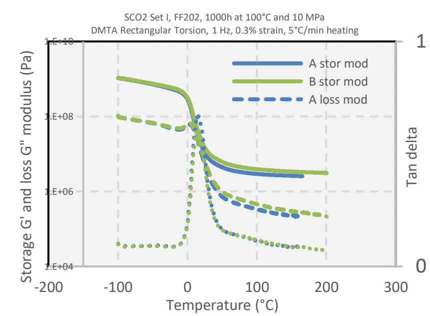
Thermoplastics (HDPE, PTFE, Nylon, PEEK, POM)

- 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

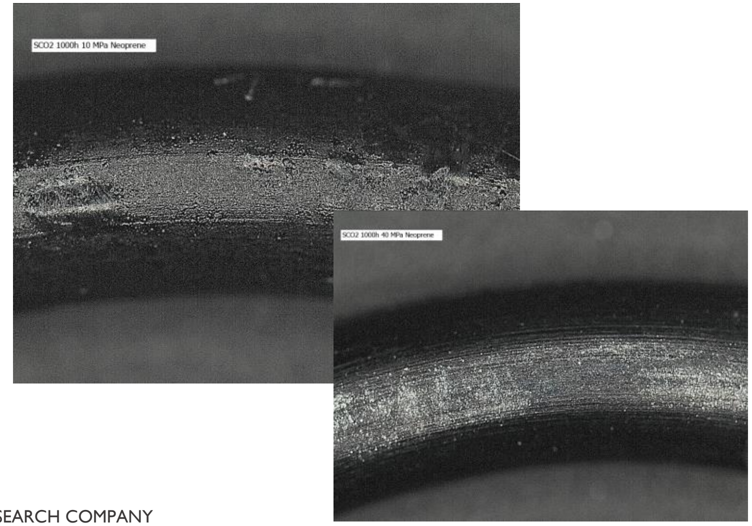
Periodic removal of O-rings at 200 hours, 600 hours and at 1000 hours followed by cutting them to characterization test specimen dimensions

* = micro-CT and nanoindentation was used selectively

Results and Discussion – Major takeaways

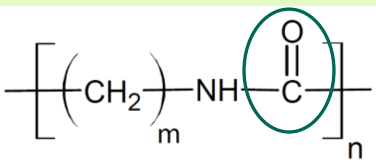
Based on experiments on 13 polymers including both elastomers and thermoplastics and under conditions of testing shared, the following are high level findings:

- **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**

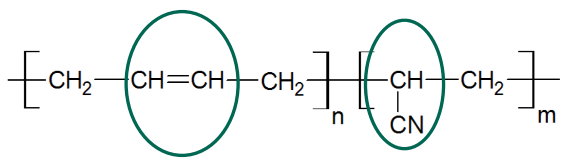


Results and Discussion – Major takeaways

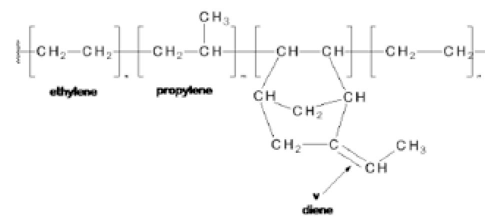
- Polymer backbone and microstructural details showed a great influence on behavior in sCO_2 environments
  - Presence of polar functionality -C=O, -C-Cl, -C-CN or -C=C- (double bonds) on backbone in polymers tested increase propensity for sCO_2 effects – for e.g. higher storage modulus with/without 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)



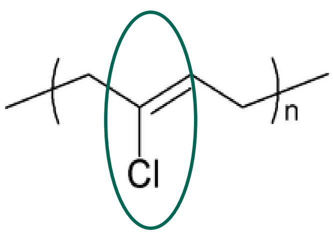
Polyamide (Nylon)



Nitrile butadiene rubber (NBR)

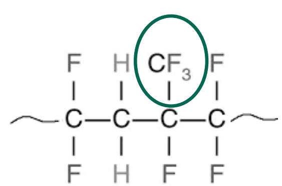


Ethylene propylene diene Monomer (EPDM)

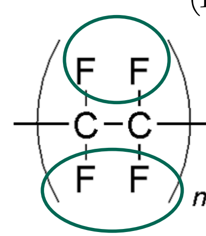


Polychloroprene (Neoprene)

FKM

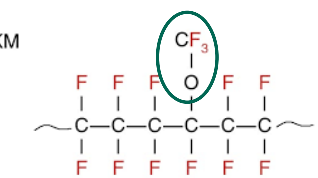


Fluoroelastomers (FKMs)



Polytetrafluoroethylene (PTFE)

FFKM

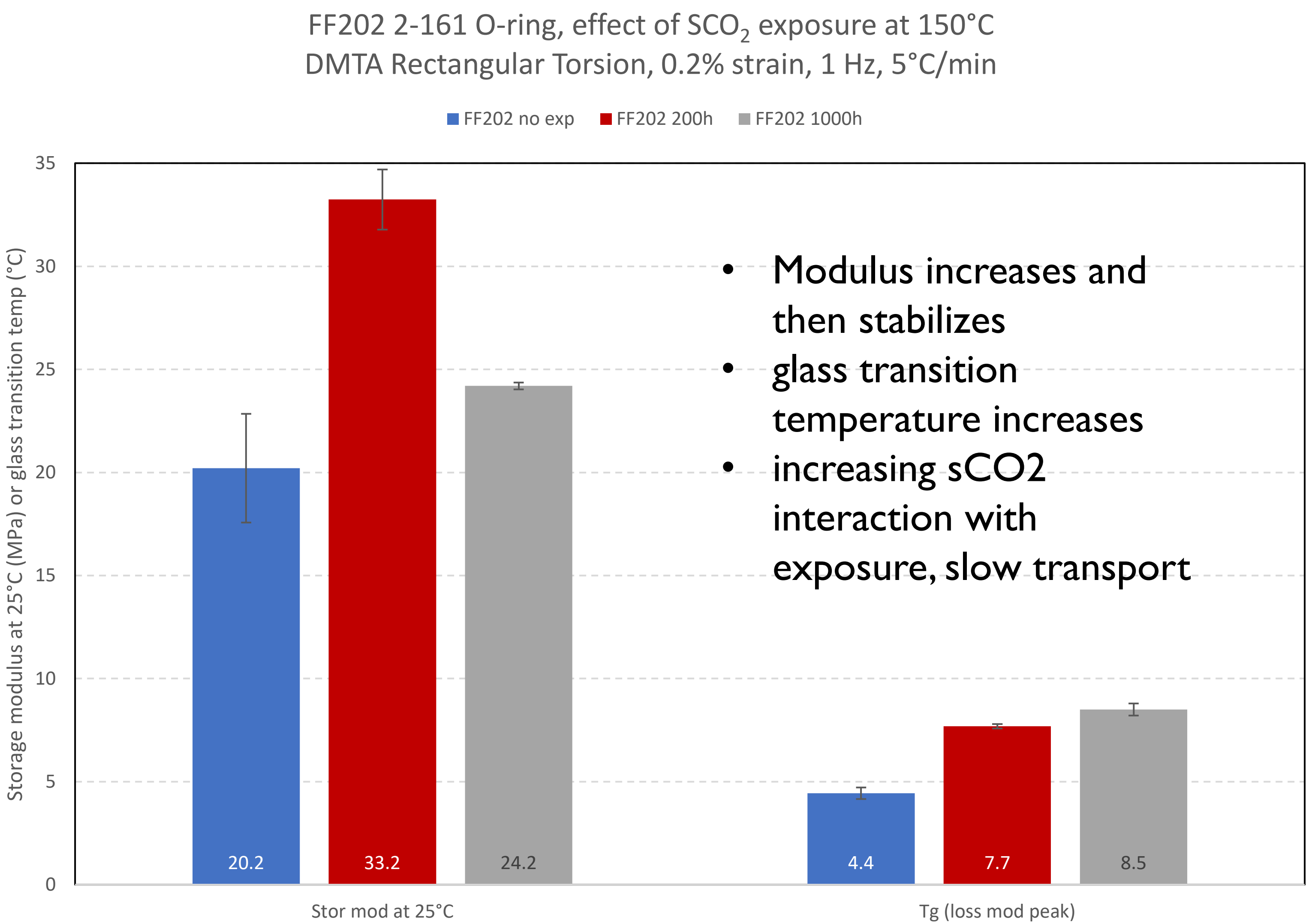


Perfluoroelastomers (FFKMs)

High level findings- Isothermal isobaric exposures of Elastomers

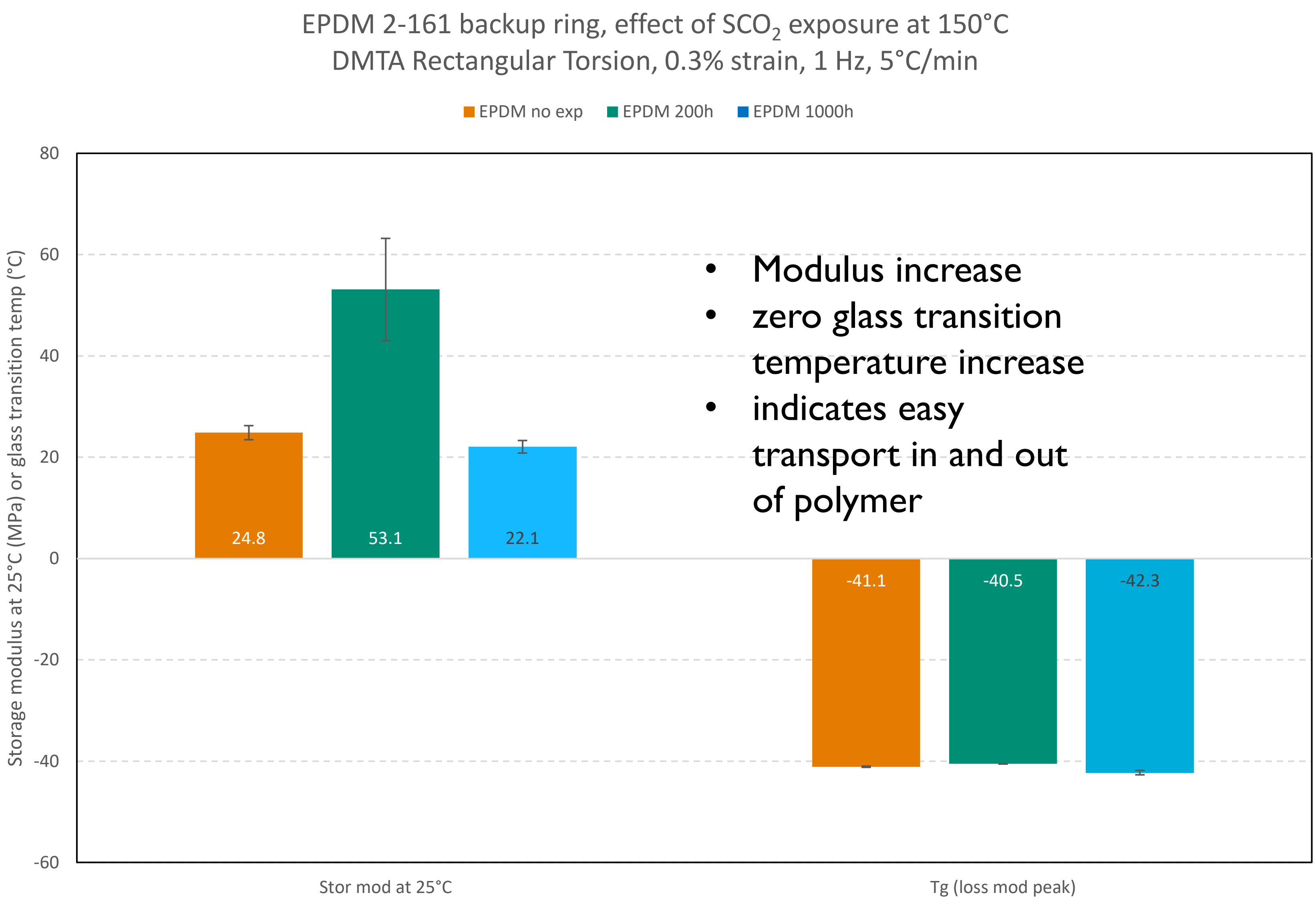
FFKM, FKM, EPDM, EPR, Buna N, HNBR, Neoprene, PUR

Dynamic Mechanical Thermal Analysis (DMTA) on FFKM FF202
150°C exposure @ 20 MPa sCO_2 pressure



- Modulus increases and then stabilizes
- glass transition temperature increases
- increasing sCO2 interaction with exposure, slow transport

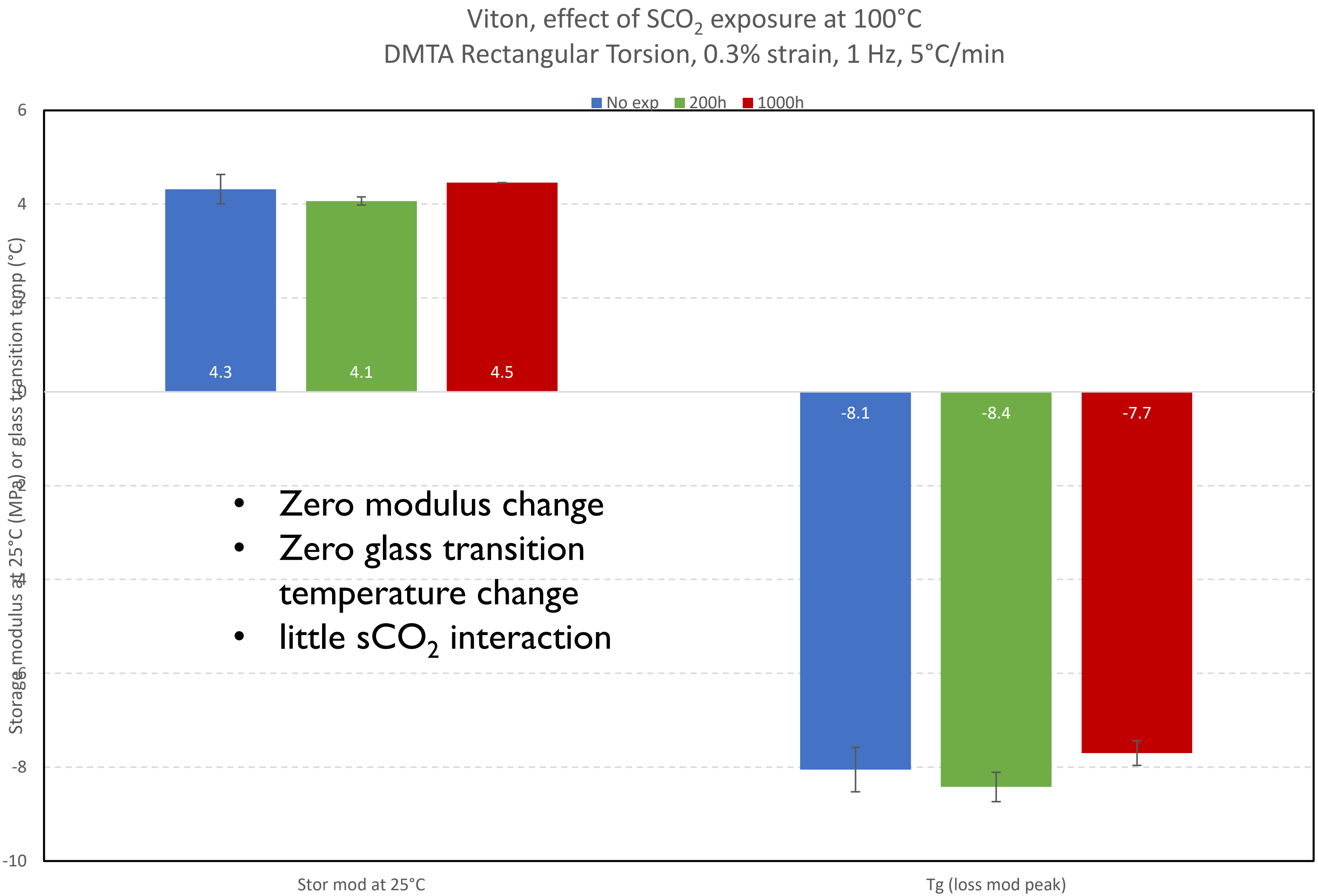
Dynamic Mechanical Thermal Analysis (DMTA) on EPDM rubber
150°C exposure @ 20 MPa sCO_2 pressure



- Modulus increase
- zero glass transition temperature increase
- indicates easy transport in and out of polymer

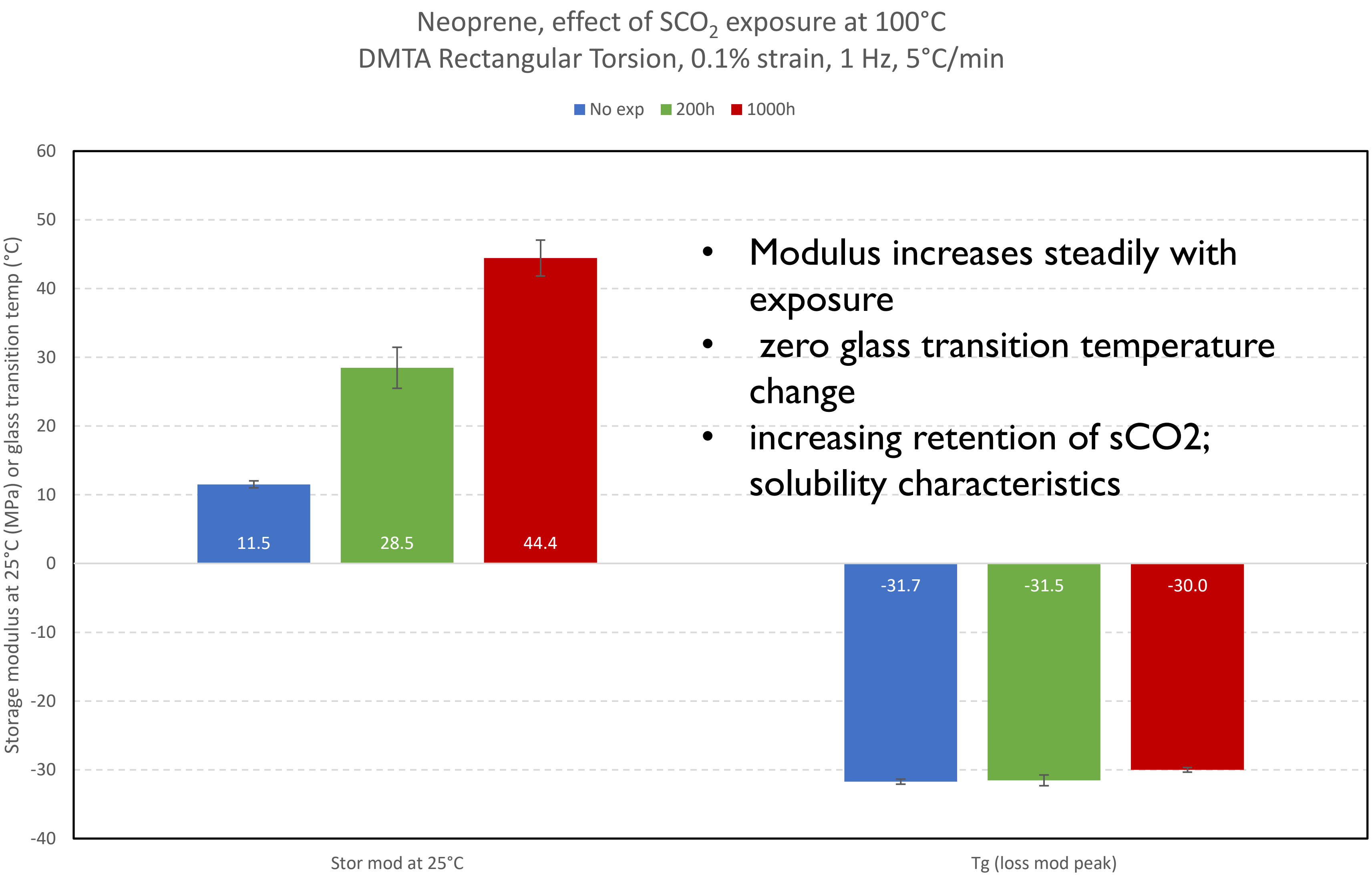
Dynamic Mechanical Thermal Analysis (DMTA) on FKM Viton

100°C exposure @ 20 MPa sCO_2 pressure



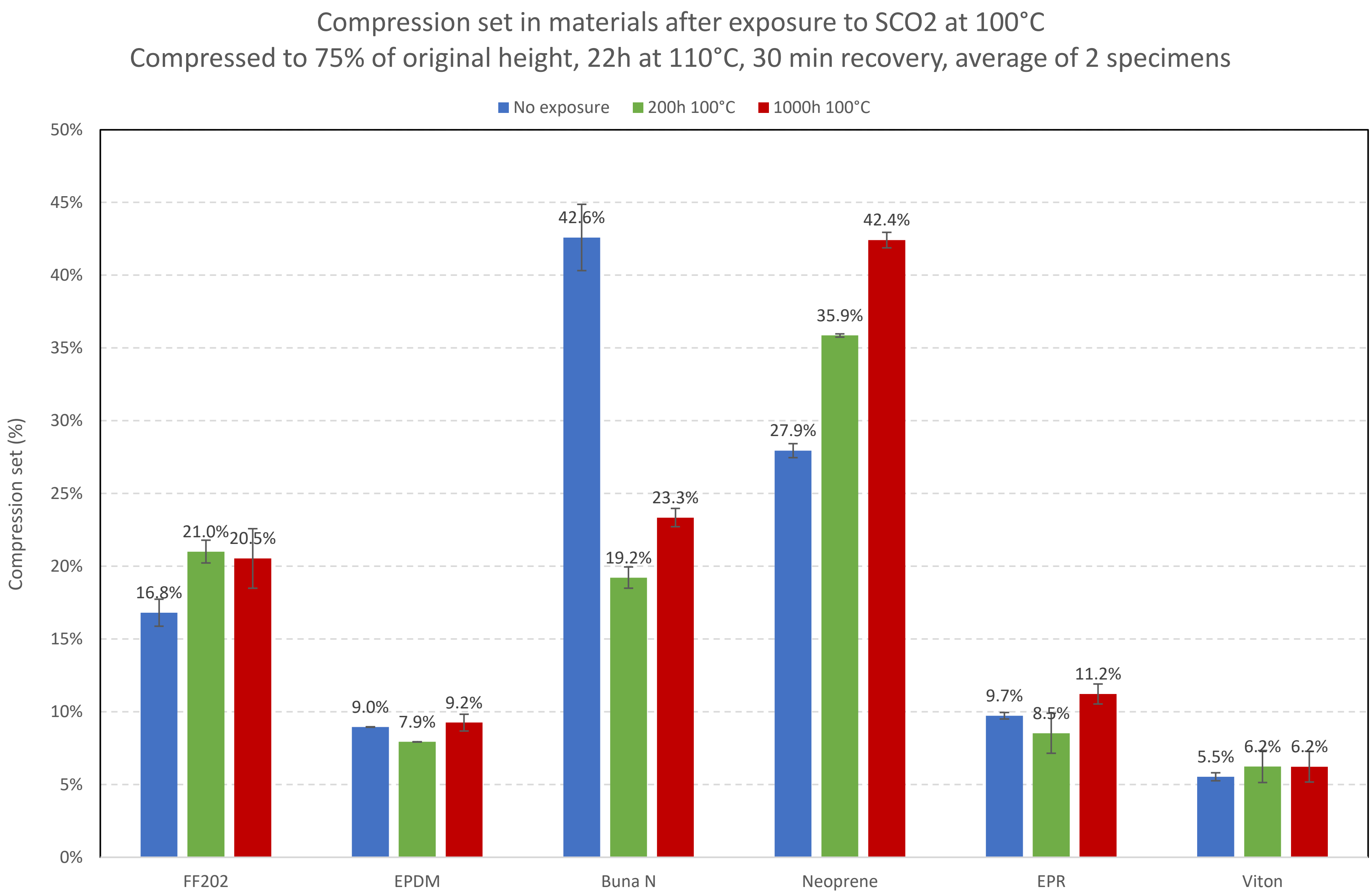
- Zero modulus change
- Zero glass transition temperature change
- little sCO_2 interaction

Dynamic Mechanical Thermal Analysis (DMTA) on Neoprene
100°C exposure @ 20 MPa sCO_2 pressure

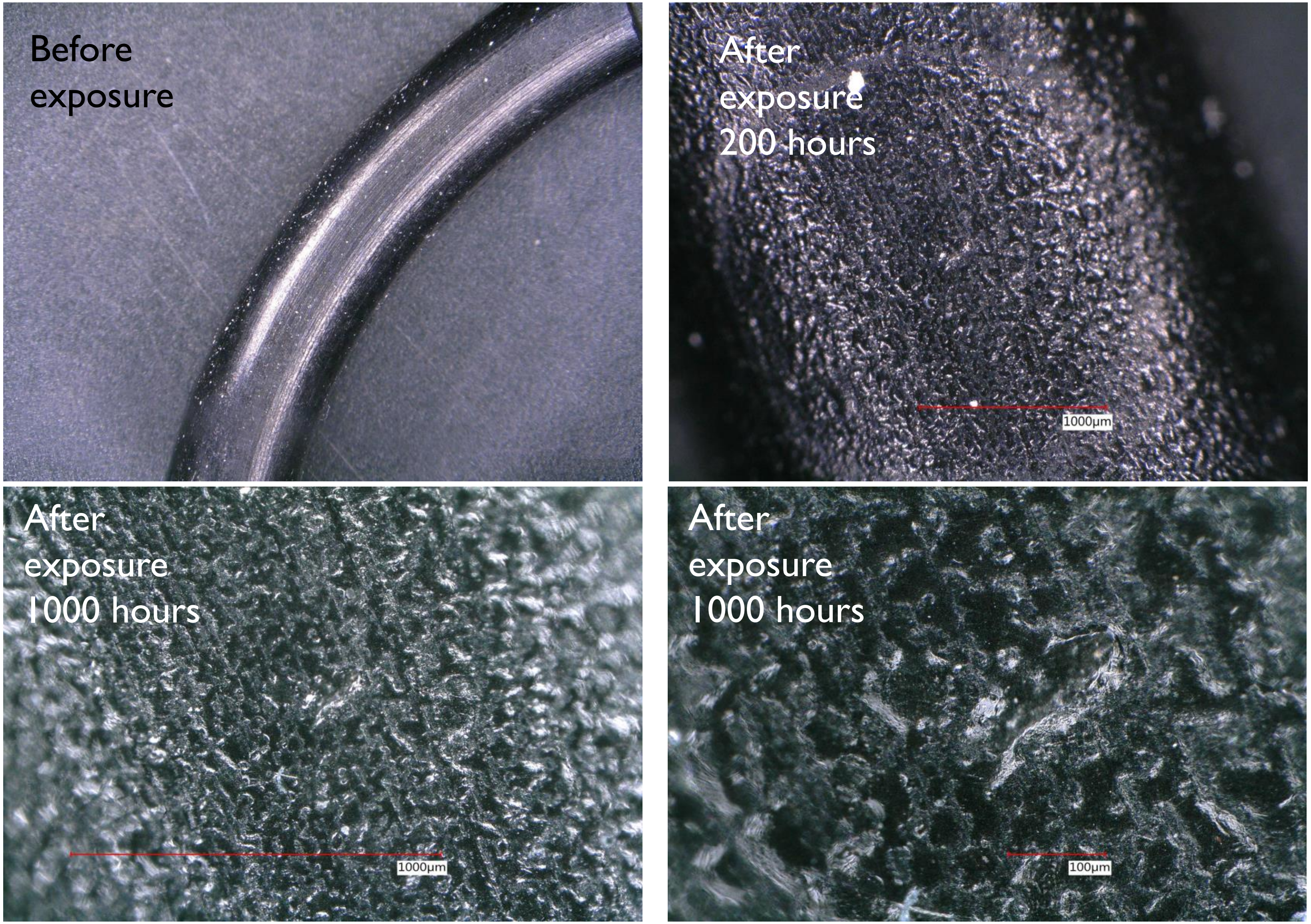


- Modulus increases steadily with exposure
- zero glass transition temperature change
- increasing retention of sCO2; solubility characteristics

Compression set (ASTM D395 method B) on different elastomers
100°C exposure @ 20 MPa sCO_2

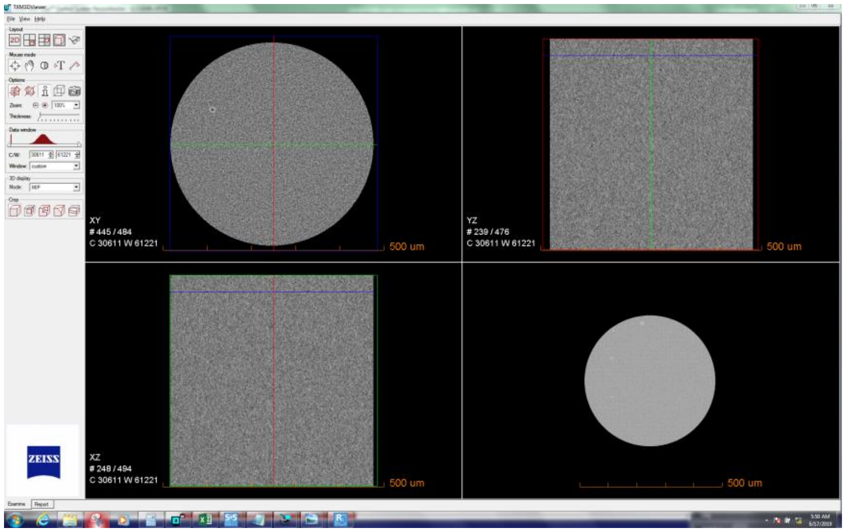


Optical microscopy images on Neoprene
100°C exposure @ 20 MPa sCO_2 pressure

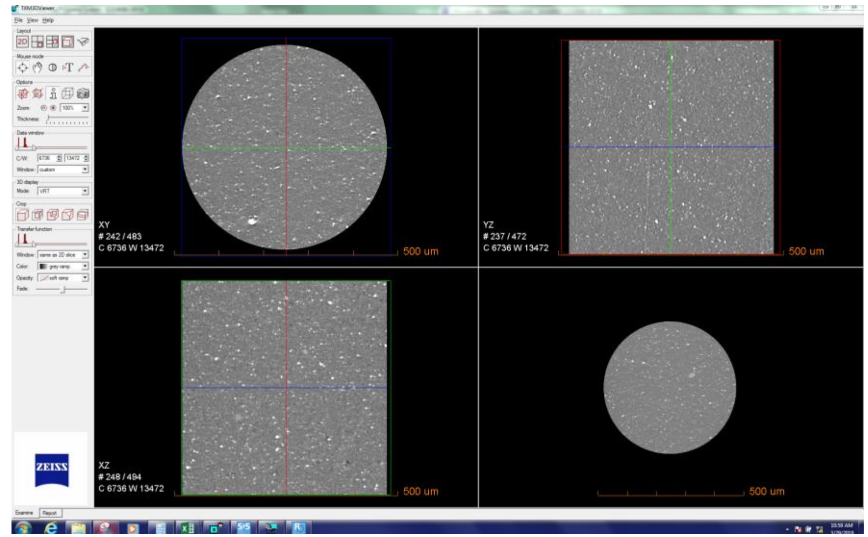


Micro-Computed tomography images for FFKM FF202 and EPDM rubbers
150°C exposure @ 20 MPa sCO_2 pressure

Unexposed

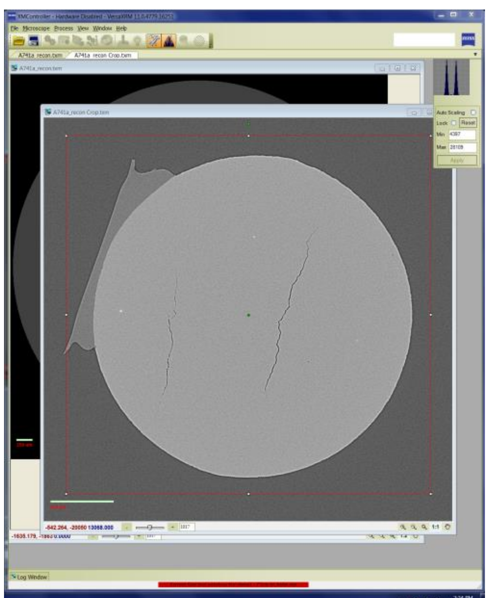


Unexposed



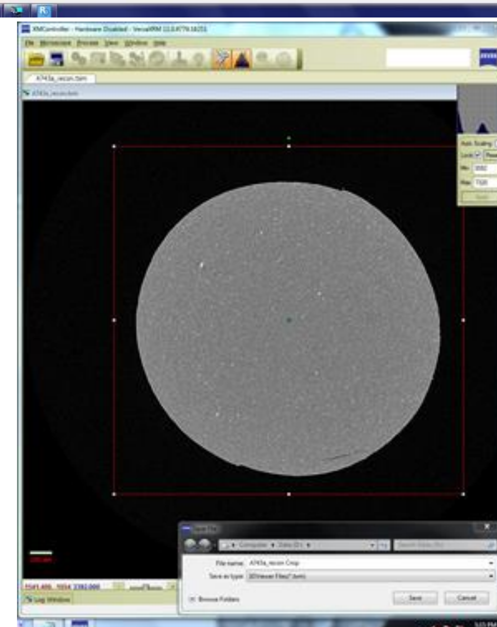
Exposed

500-1000 microns length cracks in the interior



Exposed

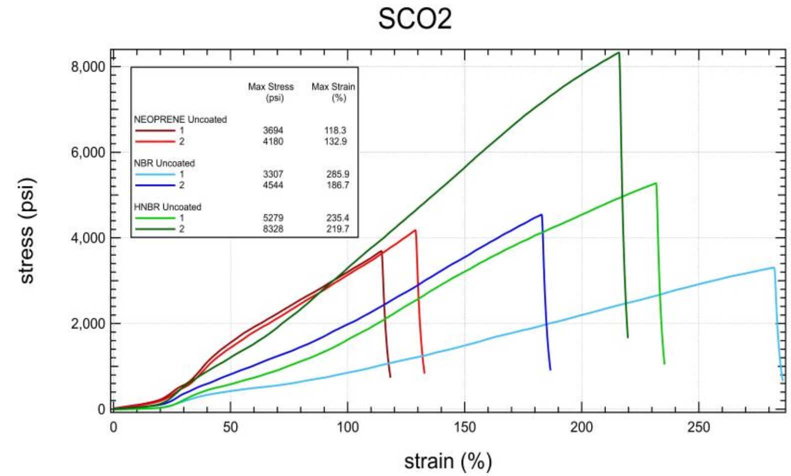
400-475 microns length cracks in the interior



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

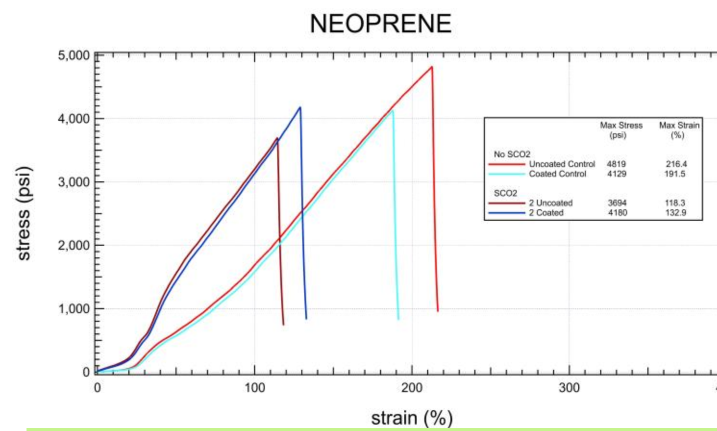
Polymers held in compression fixture during test (25% deflection)
20 MPa sCO_2 pressure at 100°C

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)

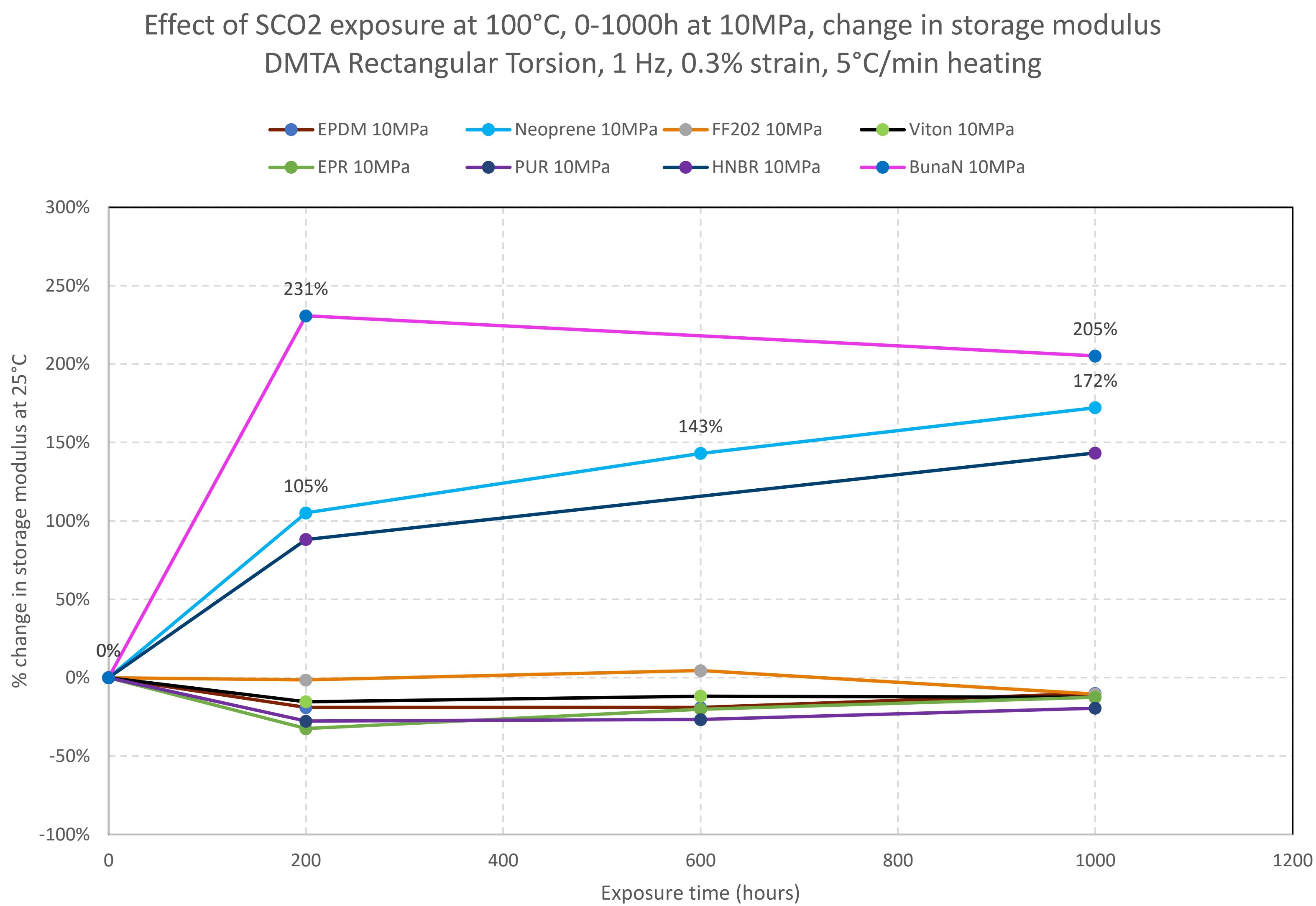


SCO_2-exposed Neoprene fails at lower % strain over unexposed

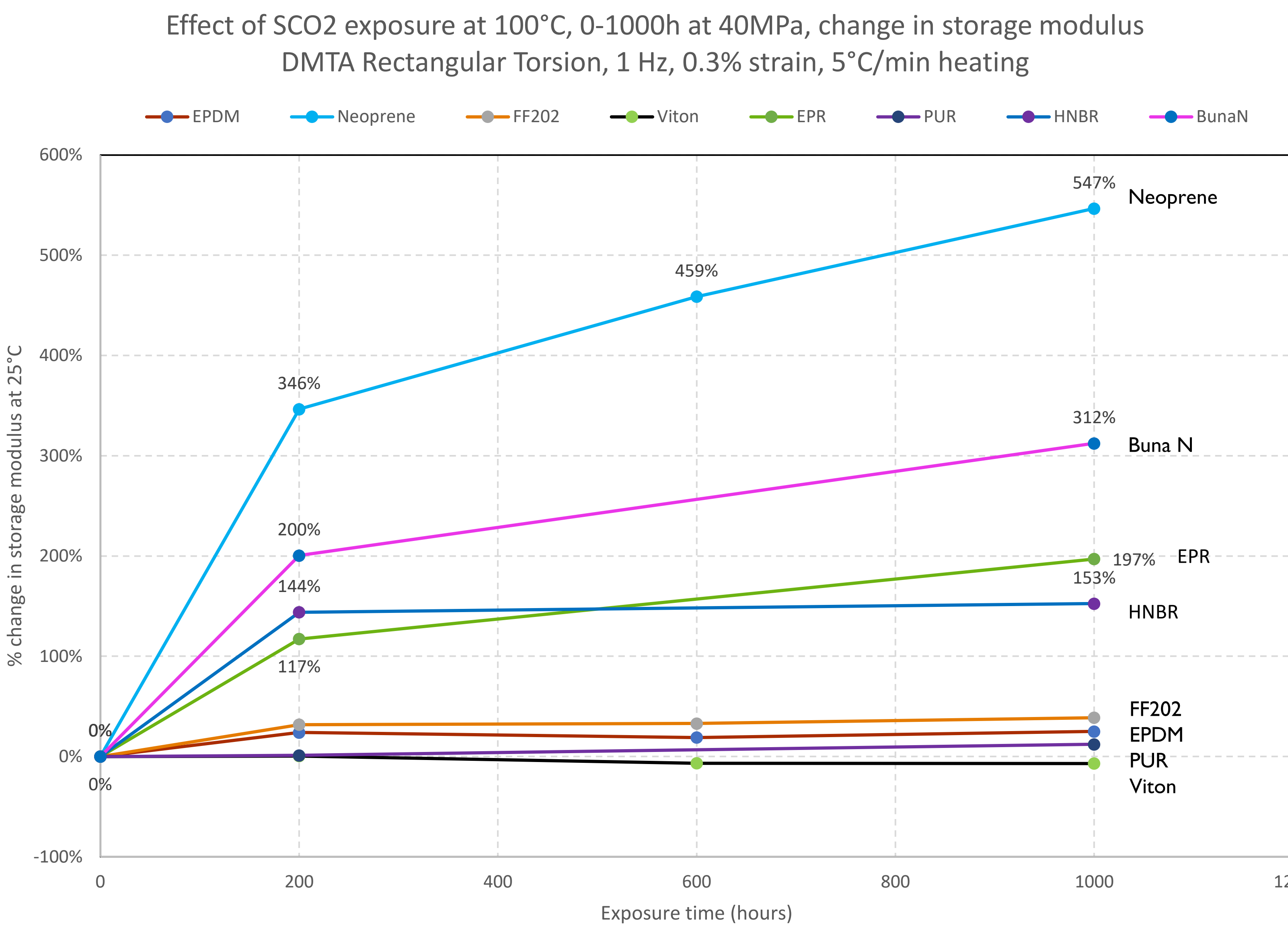
High level findings- Effect of changing pressures under isothermal conditions for Elastomers

FFKM, FKM, EPDM, EPR, Buna N, HNBR, Neoprene, PUR

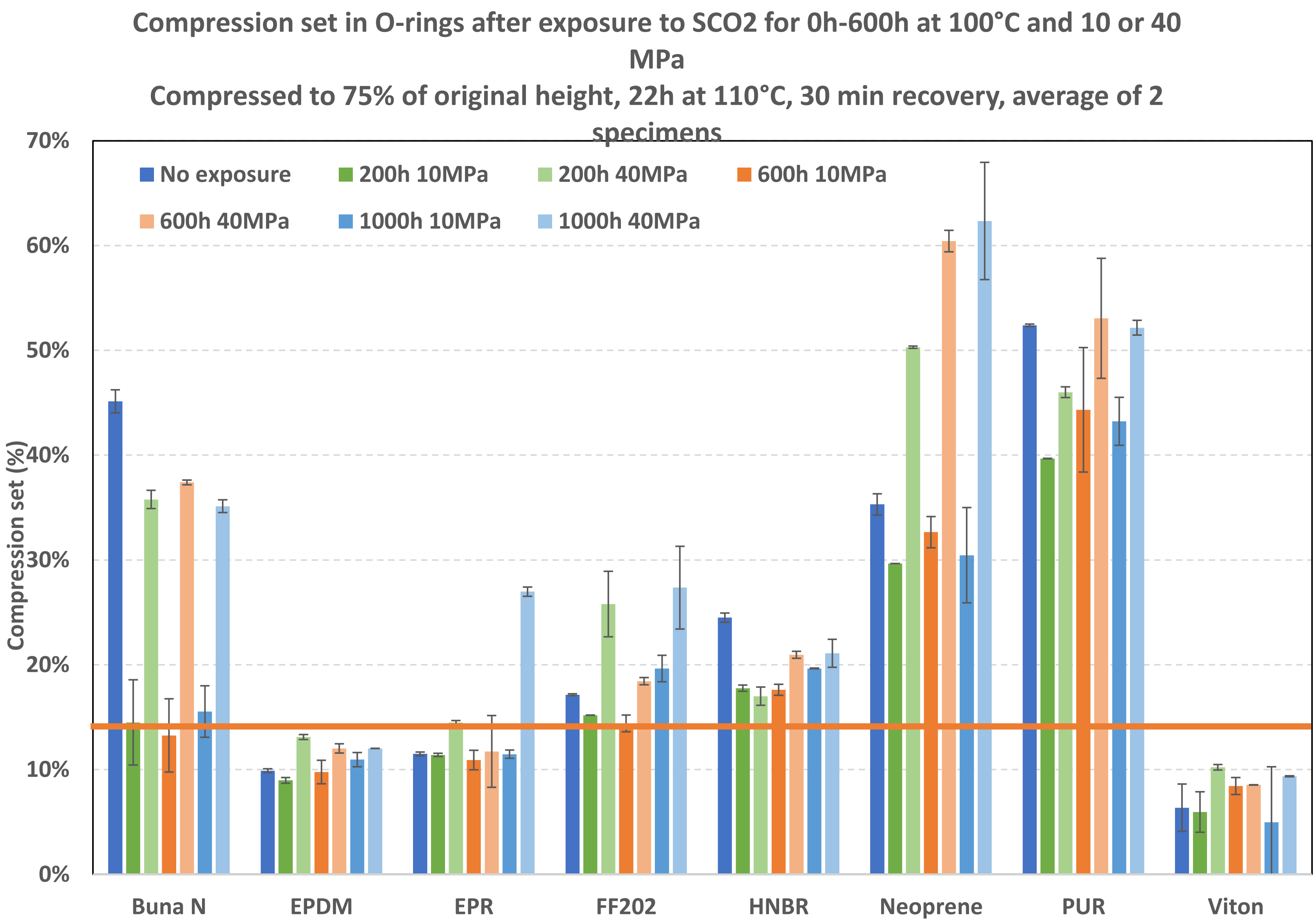
Dynamic Mechanical Thermal Analysis (DMTA) on different elastomers
Exposure to 10 MPa sCO_2 at 100°C temperature



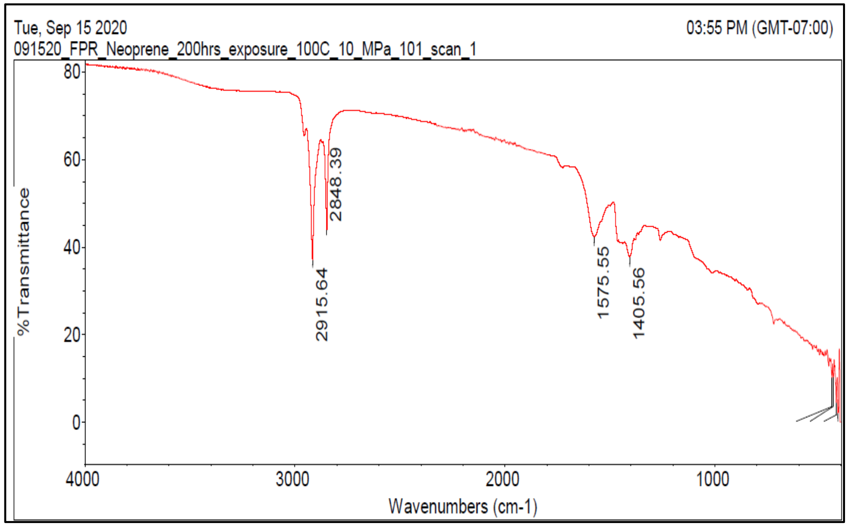
Dynamic Mechanical Thermal Analysis (DMTA) on different elastomers
Exposure to 40 MPa sCO_2 at 100°C temperature

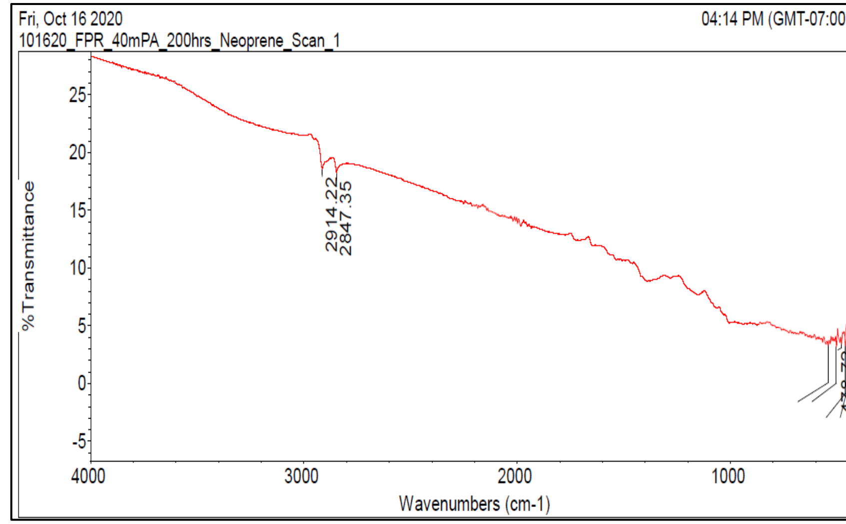


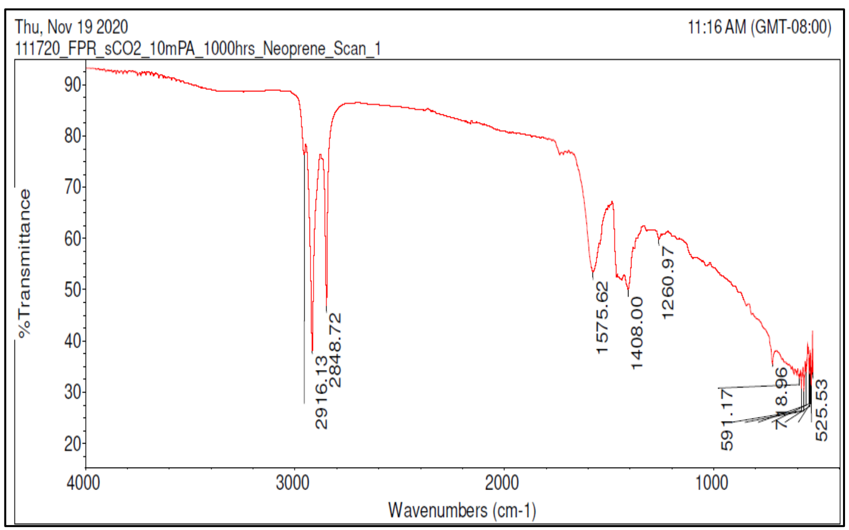
Compression set data on different elastomers
Exposure to 10 and 40 MPa sCO_2 at 100°C temperature

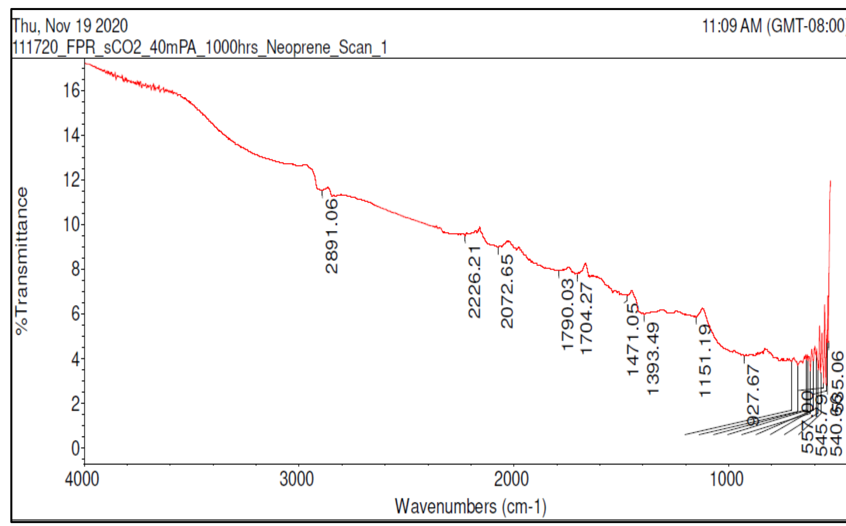


Attenuated Total Reflectance FTIR on Neoprene
Changing pressures sCO_2 at 100°C temperature







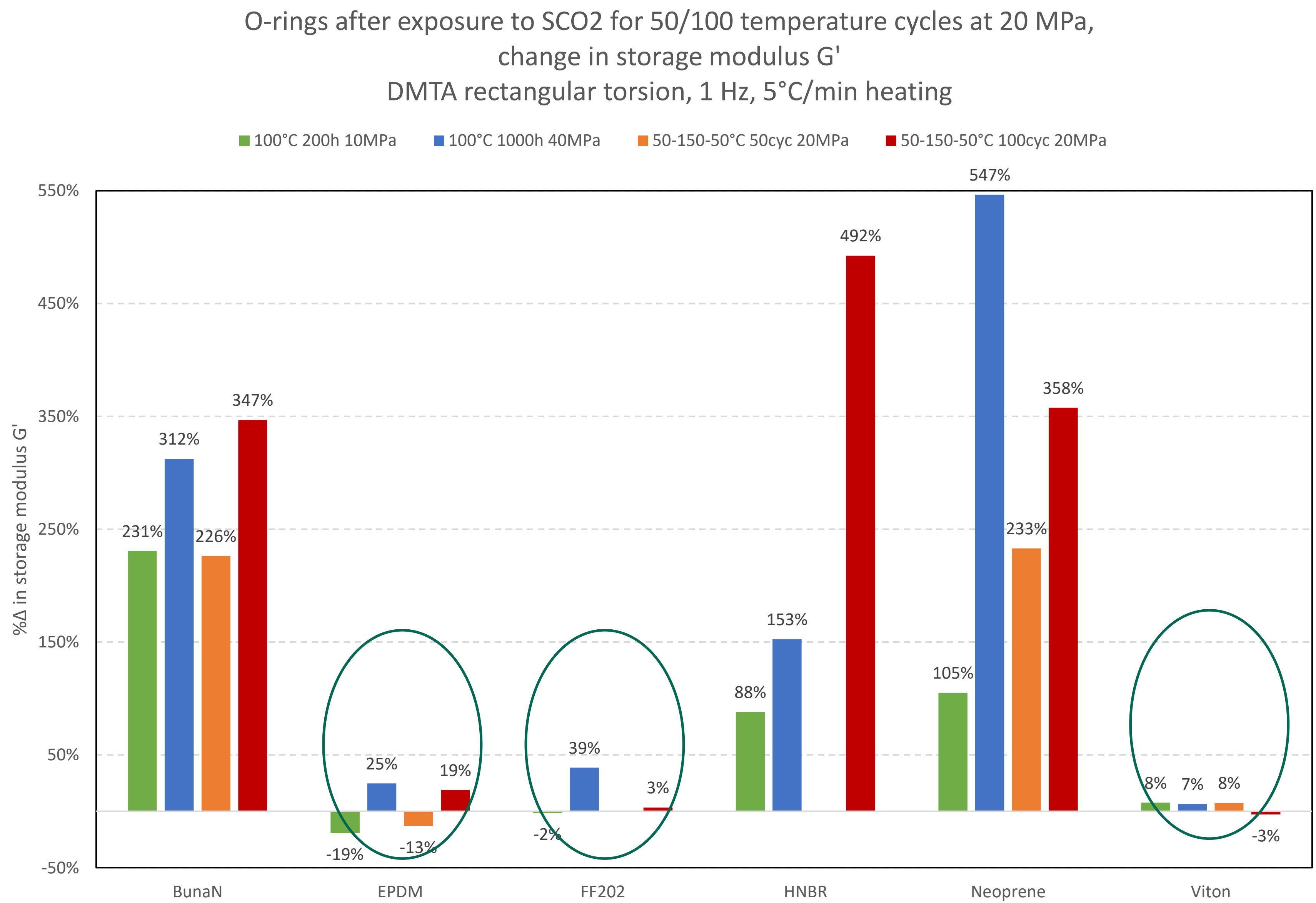


For longer exposure times (going from 200 hrs to 1000 hrs) at each pressure, peak intensity seems to increase for both pressures. Influence of pressure (10 MPa vs 40 MPa) is significant as can be seen with the decreased peak intensities.

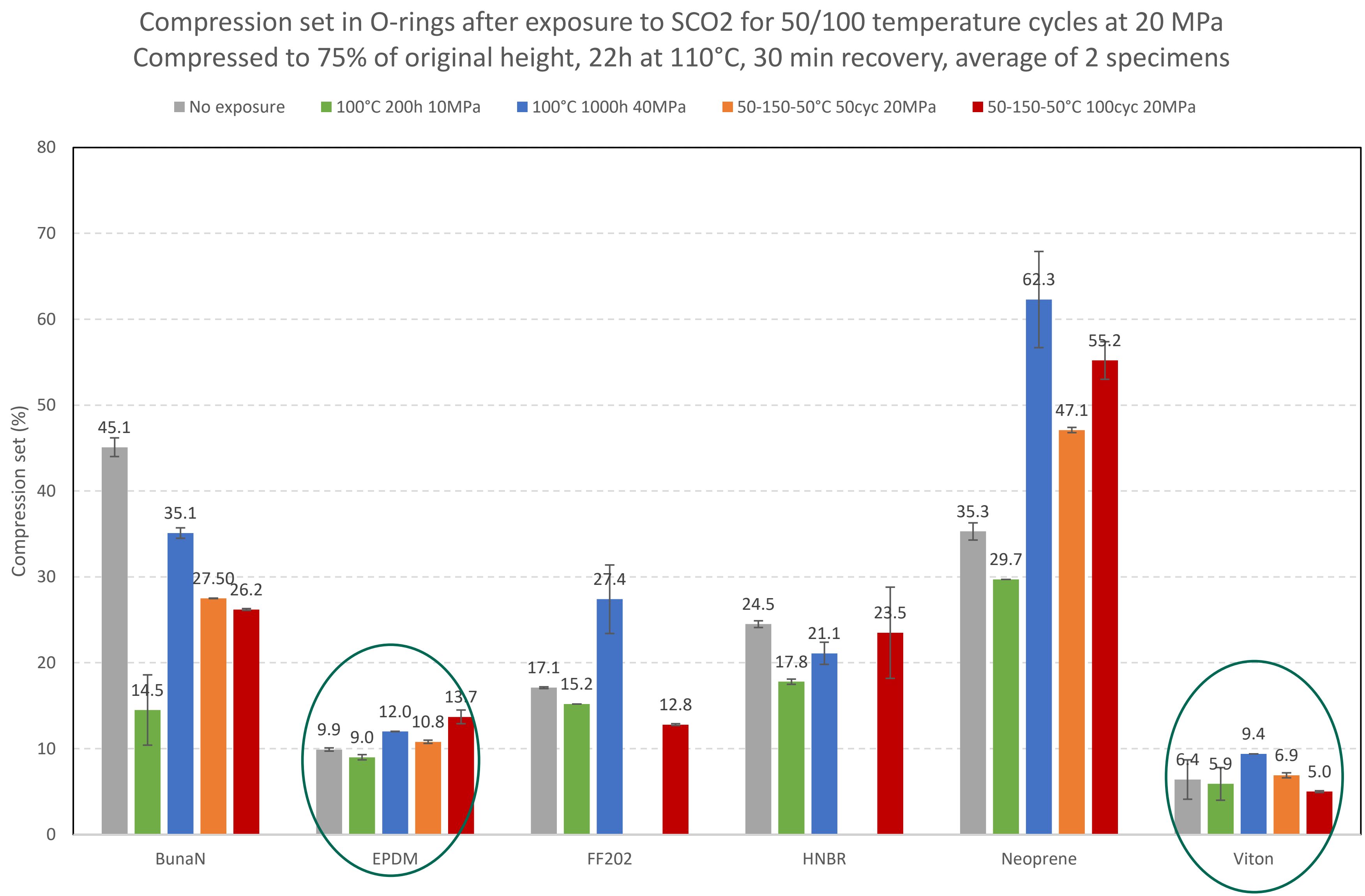
High level findings-
Isobaric thermal cycling of Elastomers

FFKM, FKM, EPDM, EPR, Buna N, HNBR, Neoprene, PUR

Dynamic Mechanical Thermal Analysis (DMTA) on different elastomers
Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure

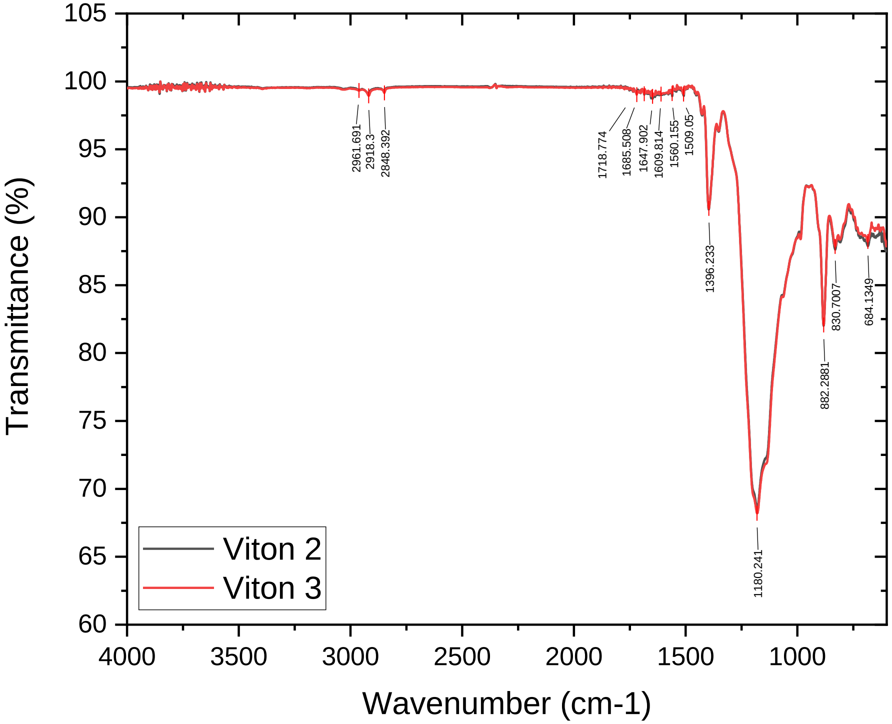


Compression set data on different elastomers
Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure

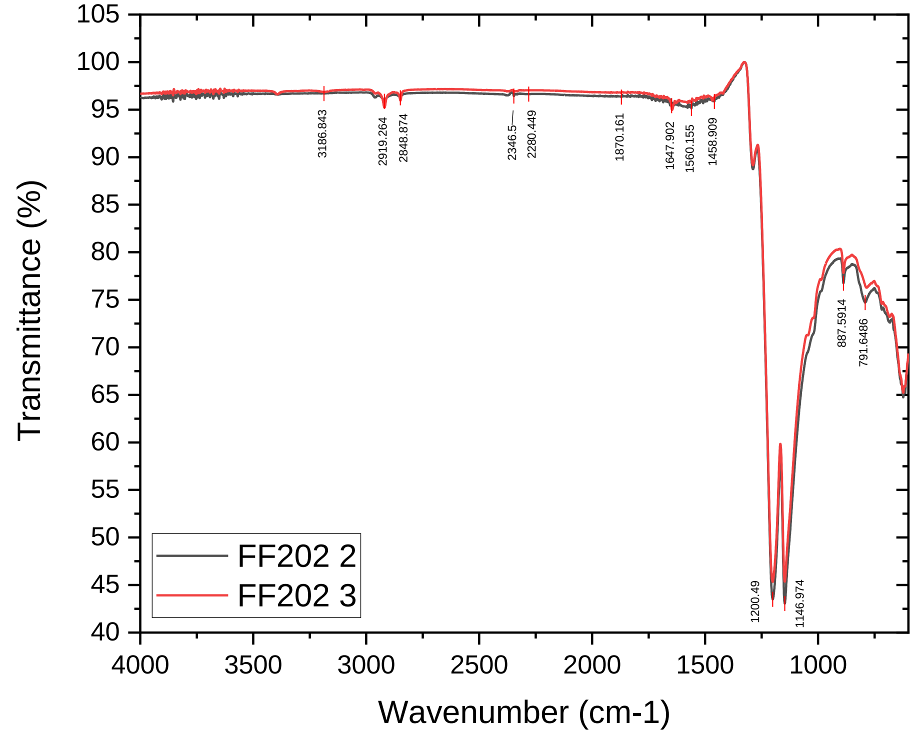


ATR-FTIR data on different elastomers
Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure

FTIR of Viton after 100 cycles of sCO2

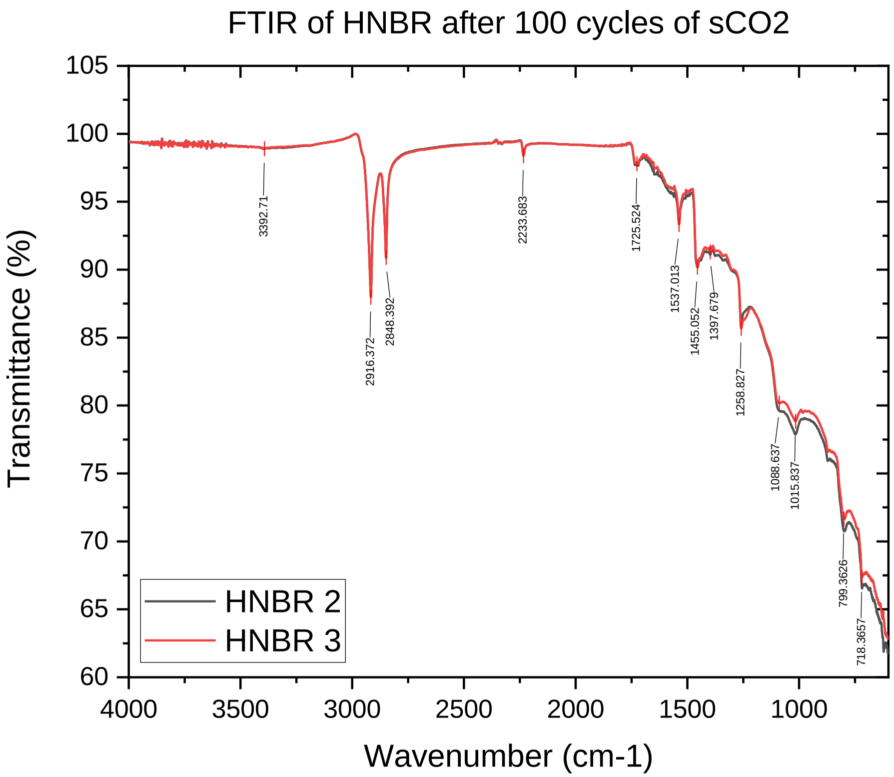


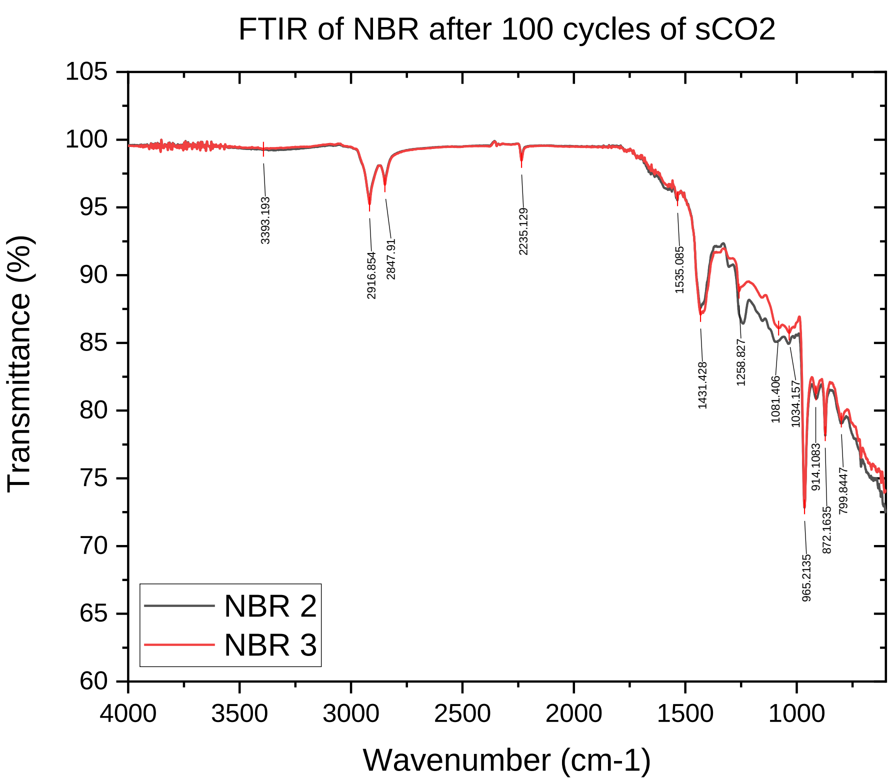
FTIR of FF202 after 100 cycles of sCO2



ATR-FTIR data on different elastomers

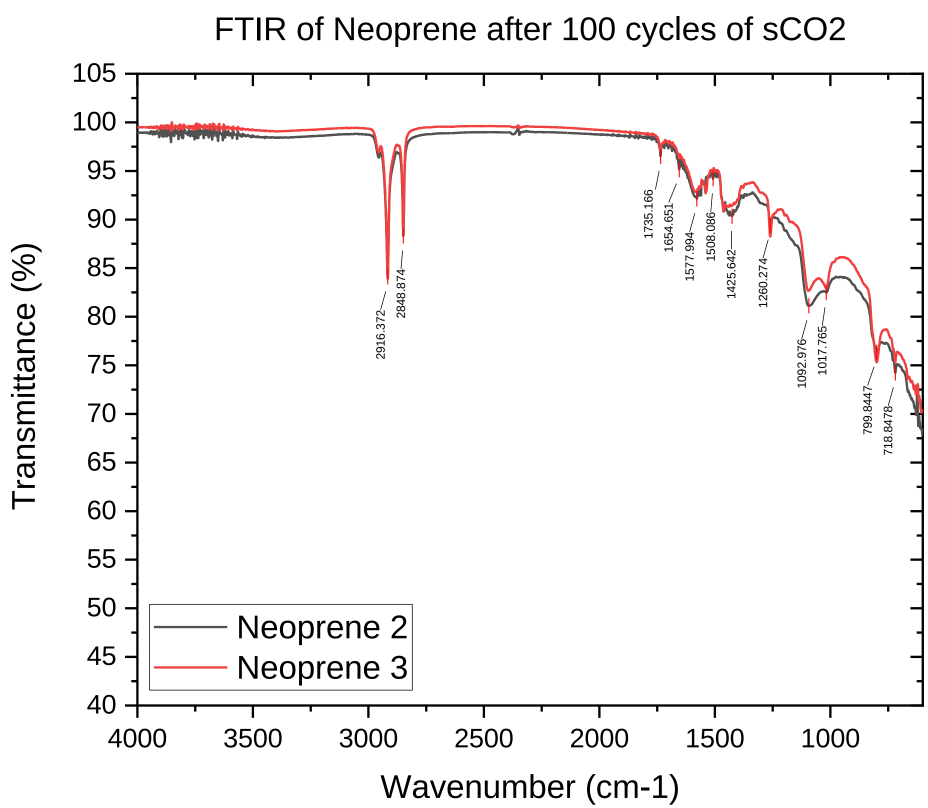
Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure

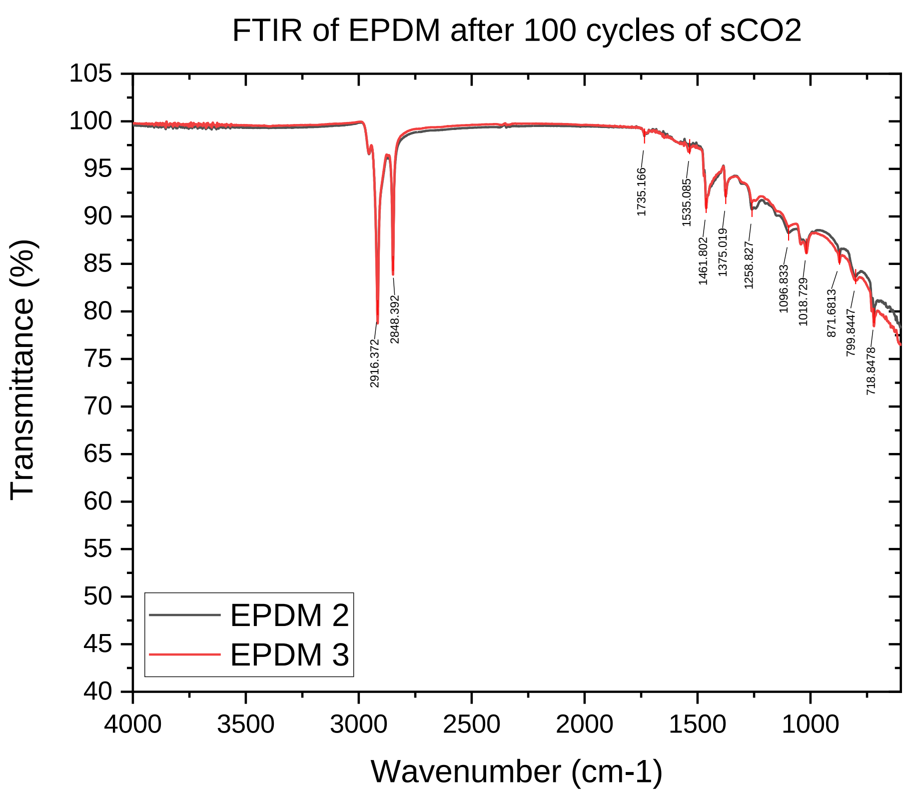




ATR-FTIR data on different elastomers

Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure



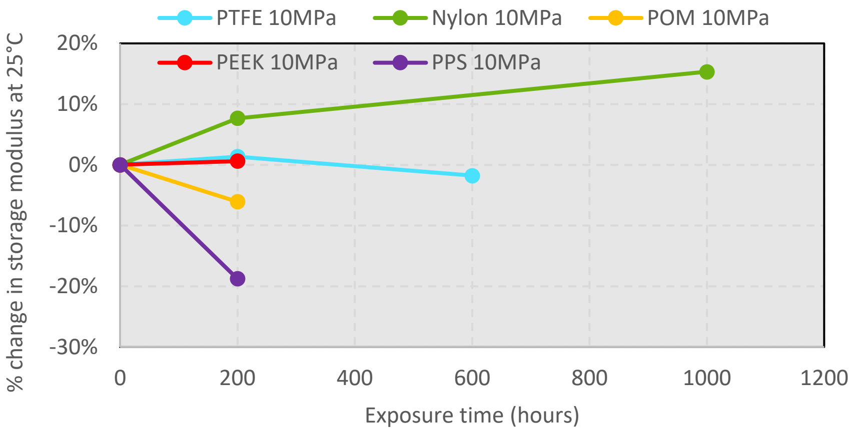


Overall trends observed with Thermoplastics for different sCO_2 exposures

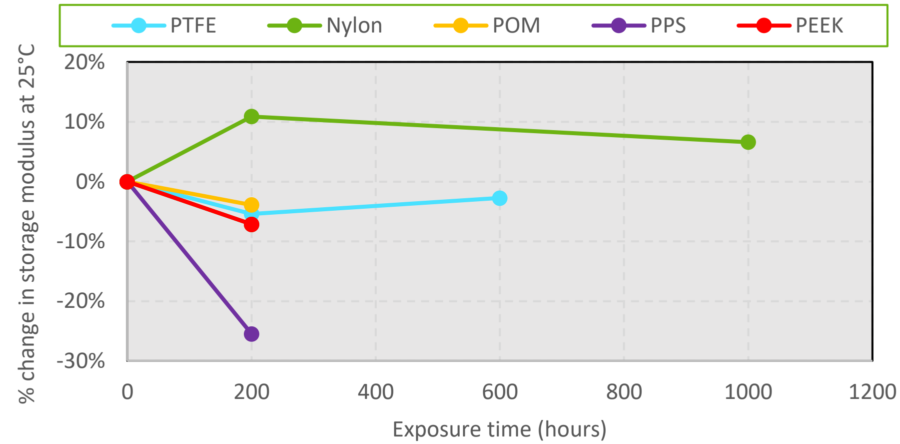
HDPE, PEEK, POM, Nylon 66, PPS, PTFE

Dynamic Mechanical Thermal Analysis (DMTA) on different thermoplastics
Exposure to 10 MPa and 40 MPa sCO_2 pressures at 100°C temperature

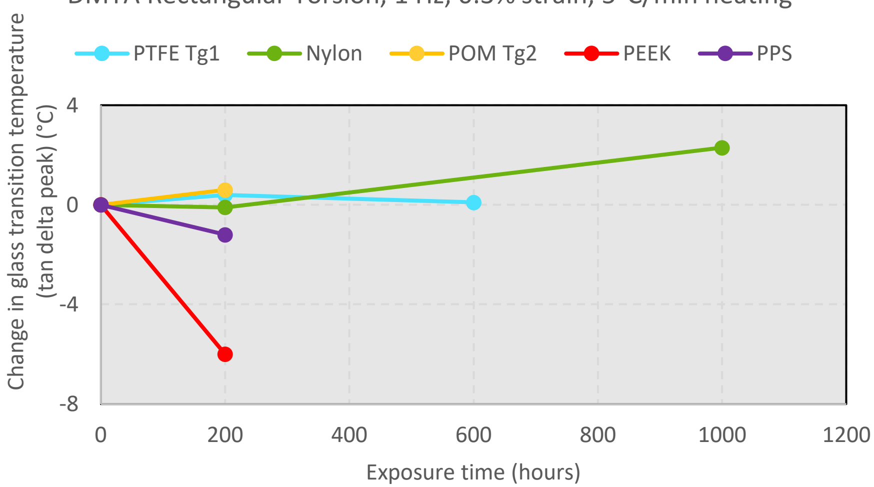
Effect of sCO2 exposure at 100°C, 0-1000h at 10MPa,
change in storage modulus
DMTA Rect. Torsion, 1 Hz, 0.3% strain, 5°C/min heating



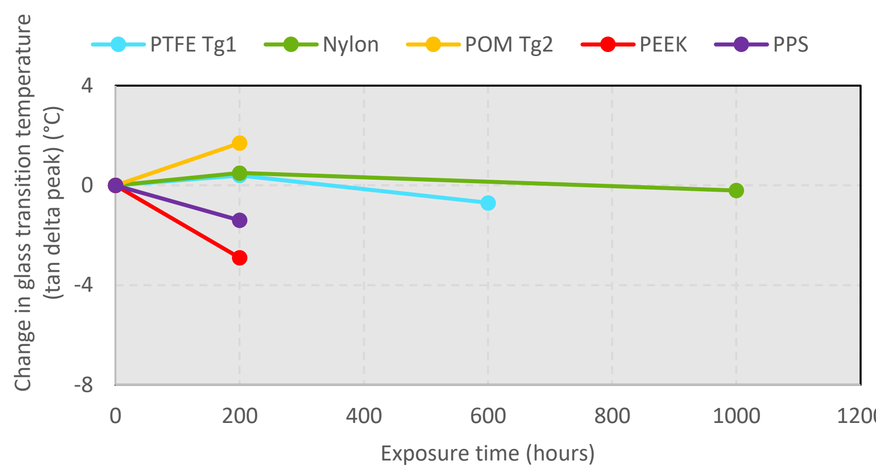
Effect of sCO_2 exposure at 100°C, 0-1000h at 40MPa,
change in storage modulus
DMTA Rectangular Torsion, 1 Hz, 0.3% strain, 5°C/min heating



Effect of sCO_2 exposure at 100°C, 0-1000h at 10MPa,
change in T_g
DMTA Rectangular Torsion, 1 Hz, 0.3% strain, 5°C/min heating

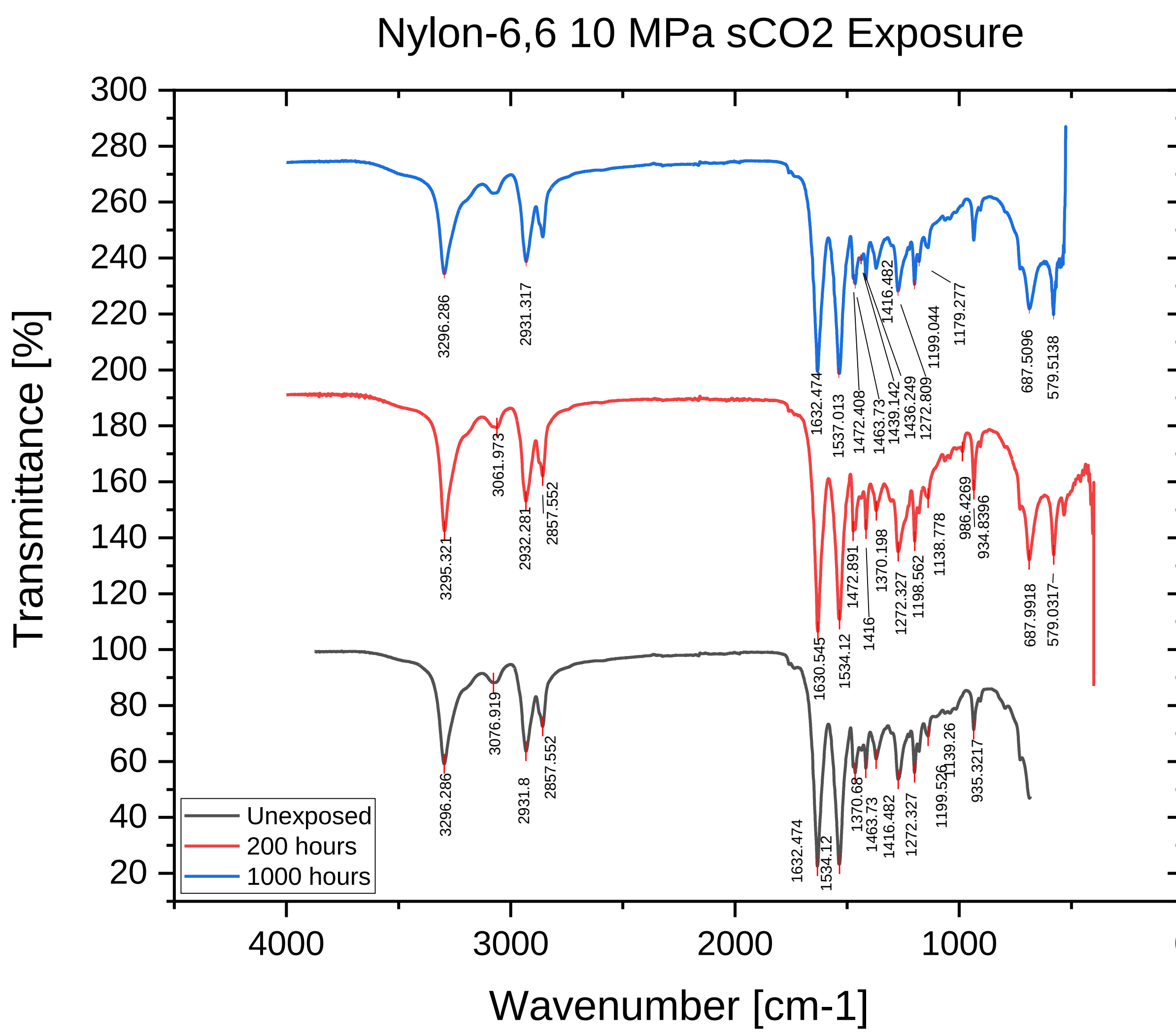


Effect of sCO_2 exposure at 100°C, 0-1000h at 40MPa,
change in T_g
DMTA Rectangular Torsion, 1 Hz, 0.3% strain, 5°C/min heating



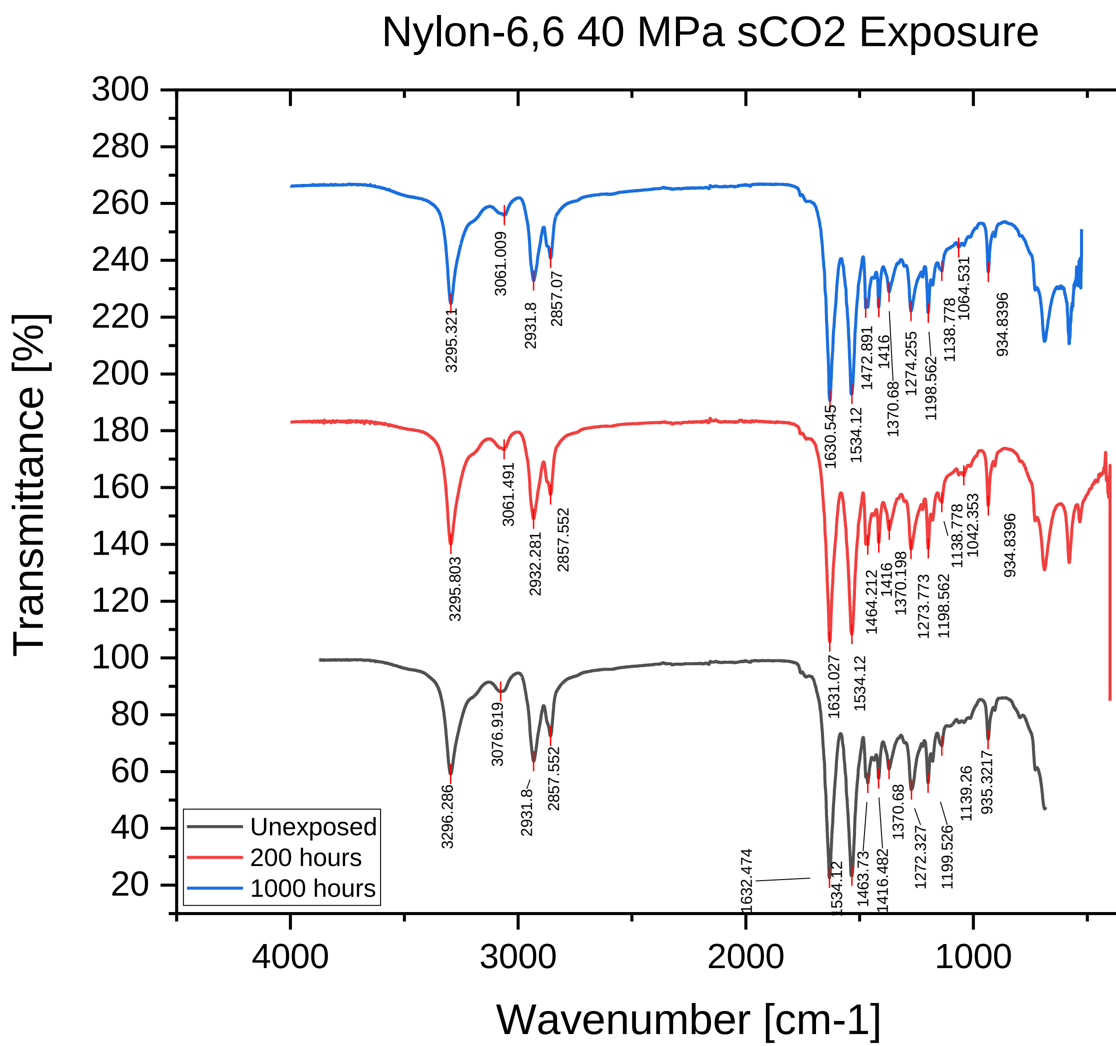
Attenuated Total Reflectance FTIR on Nylon 6,6

10 MPa pressure sCO_2 at 100°C temperature

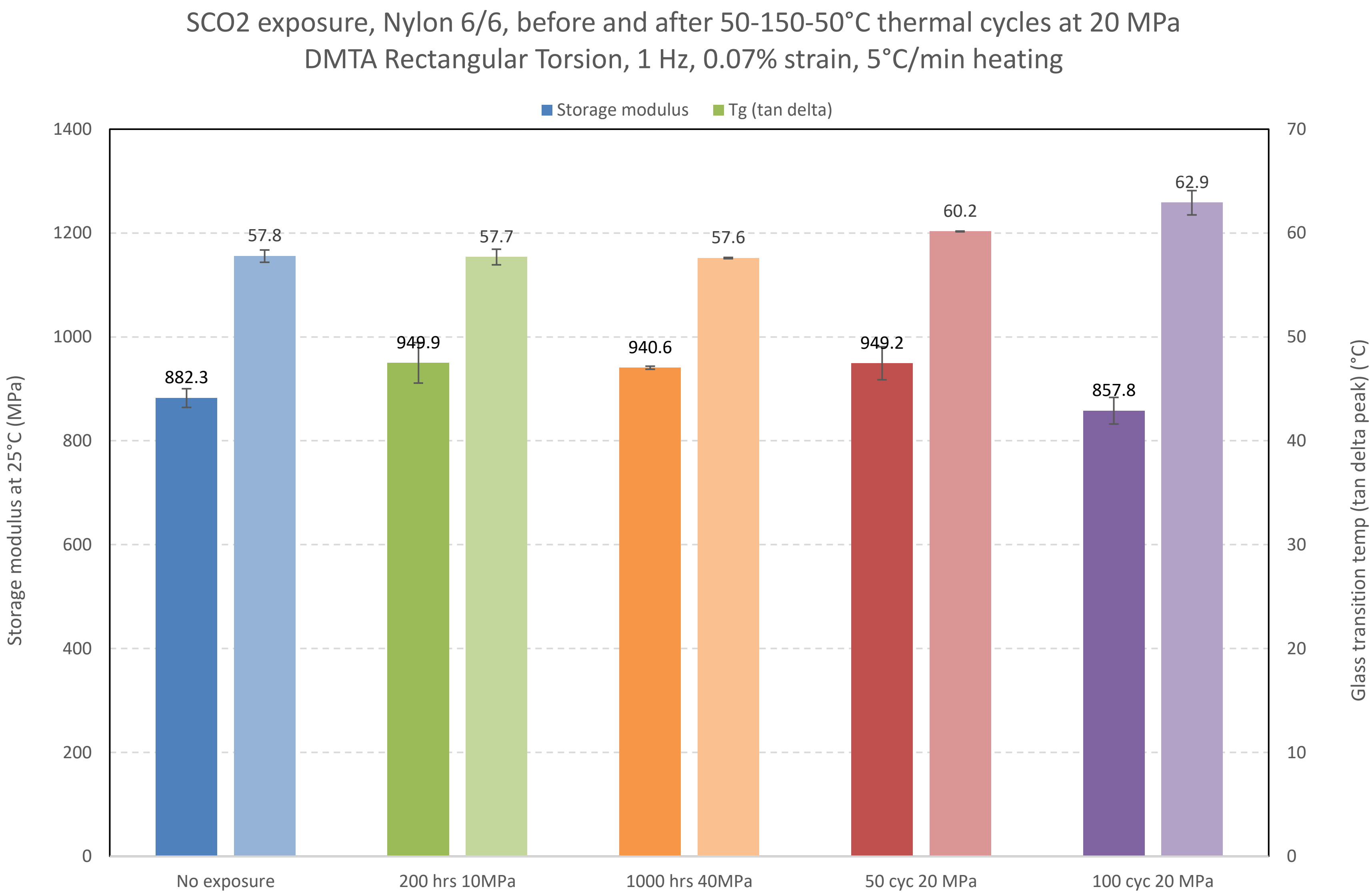


Attenuated Total Reflectance FTIR on Nylon 6,6

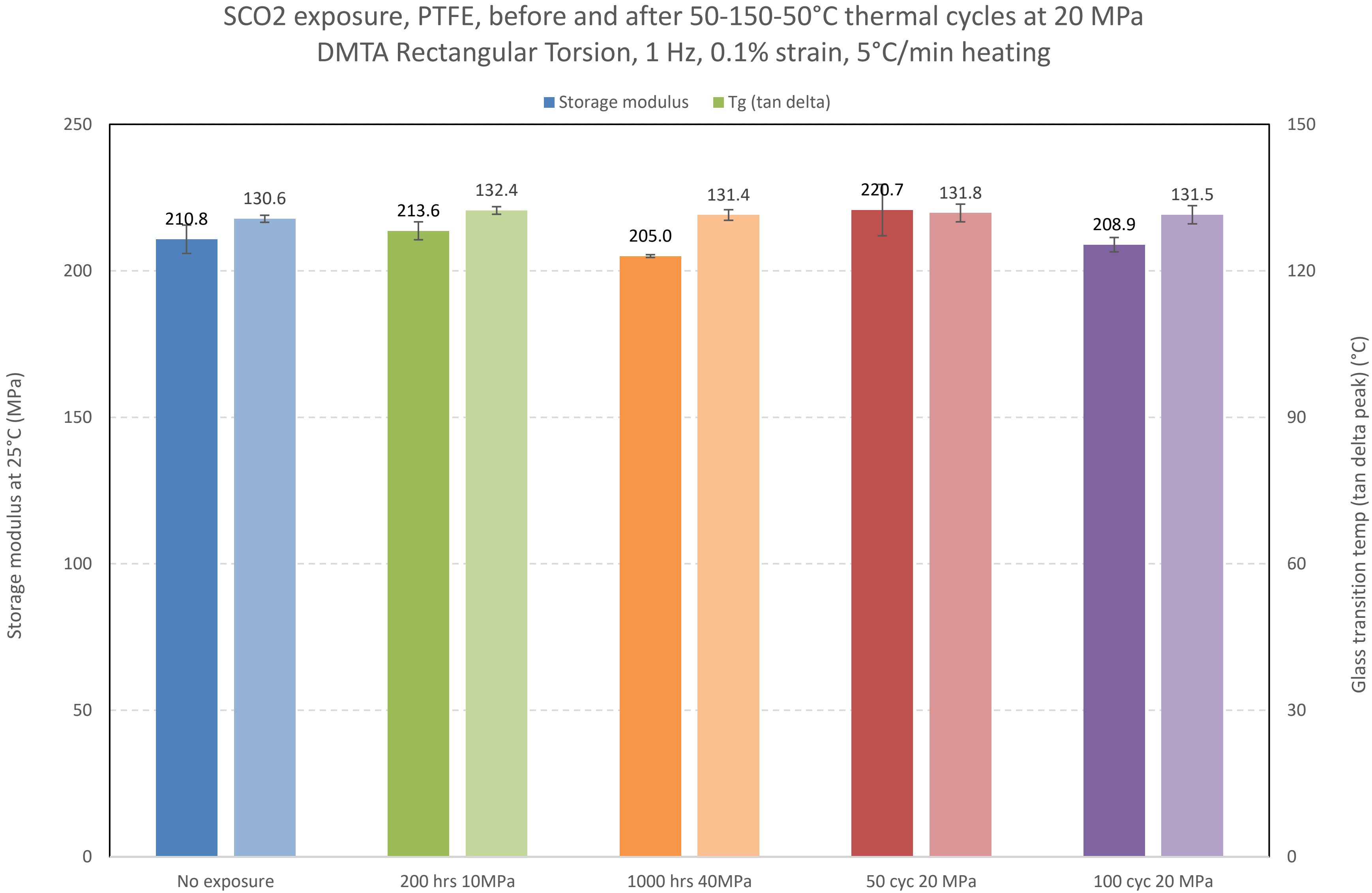
40 MPa pressure sCO_2 at 100°C temperature



Dynamic Mechanical Thermal Analysis (DMTA) on Nylon 6,6
Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure



Dynamic Mechanical Thermal Analysis (DMTA) on PTFE
Cycling from 50°-150°-50°C at 20 MPa sCO_2 pressure



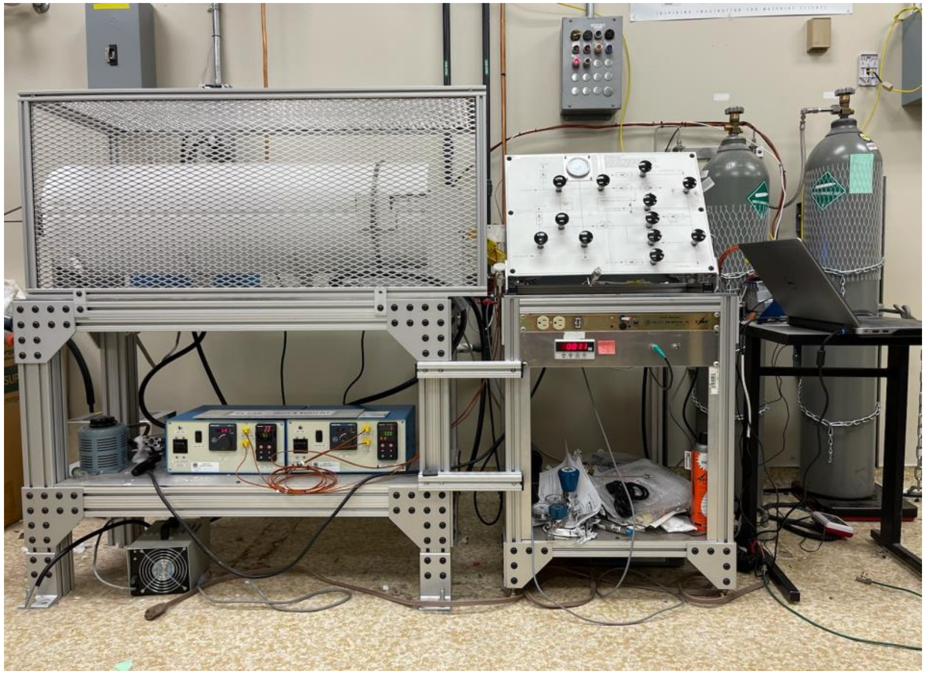
Polymer compatibility in sCO_2 –

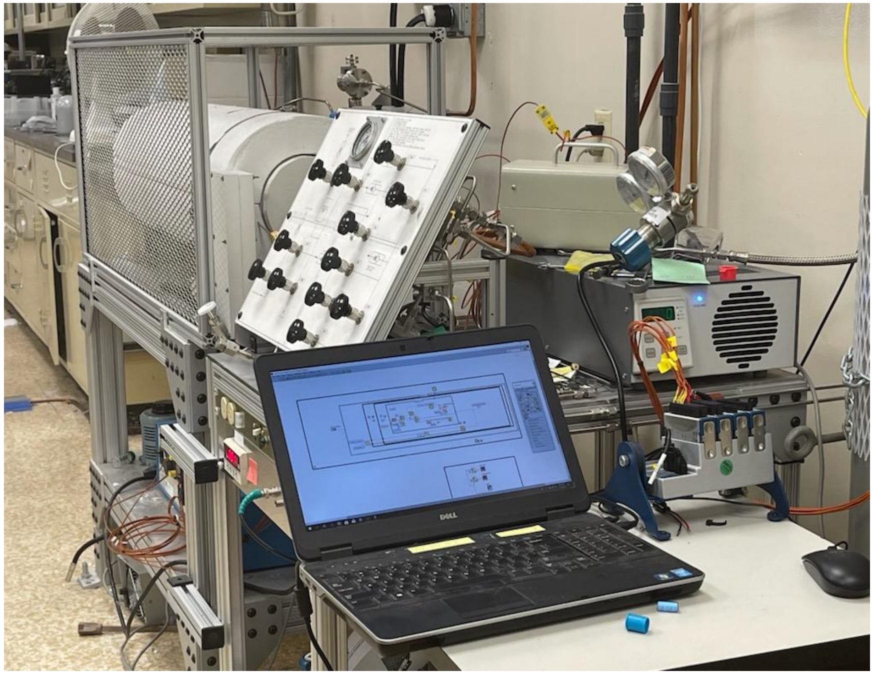
- Data for lower temperature (55-60°C) and pressure (100-1800 psig) exists; R&D required for temperature range (60-150°C) and pressures (4000-6000 psig)
- In-situ monitoring of polymer degradation and failure modes
  - polymer failure initiation and growth during the process instead of a post-mortem approach
  - Physical and mechanical property degradation studies supported by chemical characterization
- Test methods and standards development
- Cycling experiments with changes in temperature and sCO_2 pressures
- Solubility and permeation of sCO_2 in polymers and influence of fillers and plasticizers on this phenomenon
- Factors controlling rapid gas decompression – depressurization rate
- Effect of impurities such as H_2S and chemical aging of polymers
- Research and development new material resistant to sCO_2 attack

We have scratched the surface…

NEXT STEPS FY2020

- Research and development for new materials resistant to sCO_2 attack at 150°C and 250°C
- Effect of barrier coatings (metallic and non-metallic) on elastomers – high temperatures possible?
- New characterization tests to understand material degradation mechanisms
- Collaborative work and proposals for polymers and metal alloy work in sCO_2





Acknowledgements

Brian Robinson, US DOE, Office of Nuclear Energy, STEP-NE Program Manager

Gary Rochau (Retired), Sandia National Labs, Sandia STEP Program Manager

Carmen Margarita Mendez, Sandia National Labs, STEP Program Manager

Erica Larson, Project Controller

Bonnie Antoun, Sandia National Labs, sCO2 Materials Development Co-Lead

Chris Reed, Sandia National Labs, Technical support for optical microscopy

Bernice Mills, Sandia National Labs, Technical support for micro CT

Jeff Campbell, Sandia National Labs, Technical support for autoclave operations

Gwyneth Diaz, Sandia National Labs, Technical support for mechanical testing

Adriana Pavia, Sandia National Labs, Technical support for ATR-FTIR expertise


THANK YOU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