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Compatibility of polymers in super-critical carbon dioxide for power generation systems under low temperatures and pressure conditions

N. Menon[1], M. Walker[1], N. Colgan[2], M. Anderson[1], A. Nissen[1], and L. Massey[3]

[1] = Sandia National Laboratories, CA ; [2] = University of Wisconsin, Madison; [3] = Sandia National Laboratories, NM

ABSTRACT

Polymers such as PTFE (polytetrafluorethylene or Teflon), PEEK (polyetheretherketone), EPDM (ethylene propylene diene monomer) rubber, Viton, EPR (ethylene propylene rubber), Nylon, Nitrile rubber, and perfluoroelastomers are commonly employed in super critical CO_2 (sCO2) energy conversion systems. O-rings and gaskets made from these polymers face stringent performance conditions such as elevated temperatures, high pressures, pollutants and corrosive humid environments. Critical knowledge gaps about polymer degradation from sCO2 exposure need to be addressed. To understand these effects, we have studied nine commonly used polymers (PEEK, Nylon, PTFE, EPDM, Nitrile rubber, EPR, Neoprene, perfluoroelastomer FF 202 and Viton) at elevated temperatures under isobaric conditions of sCO2 pressure. The polymers were exposed for 1000 hours at 100°C to 20 MPa sCO2 pressure in an autoclave. In a second study, elastomers perfluoroelastomer (FF202) and EPDM were exposed to 20 MPa sCO2 for 1000 hours at 150°C. Samples were extracted for ex-situ characterization at t = 200 hours and then at the completion of the test at t=1000 hours. The polymer samples were examined for physical and chemical changes by Dynamic Mechanical and Thermal Analysis (DMTA), Fourier Transform Infrared (FTIR) spectroscopy, and compression set. Density and mass changes immediately after removal from test and 48 hours later, and optical microscopy techniques were also used. Microcomputer tomography (micro CT) data was generated on select specimens. Super-critical CO_2 effects have been identified as either physical or chemical effects. For each polymer, the dominance of one type of effect over the other was evaluated. Attempts were also made to qualitatively link sCO2 effects such as lowering or increase in glass transition temperatures, storage modulus changes, mass and compression set changes, chemical changes seen in FTIR analyses and blister and void formation seen post-exposure to polymer microstructure-related mechanisms such as plasticization of the polymer matrix, escape of volatiles from the polymer during depressurization, and filler and plasticizer effects on microstructure with rapid depressurization rates.

1. INTRODUCTION

Carbon dioxide in its super-critical fluid state (Figure 1) is used in energy conversion systems because it can expand as a gas with the density of a liquid which enables lower pumping power needed in a compressor, thus increasing the thermal-to-critical energy conversion efficiency (source: https://energy.sandia.gov/energy/renewable-energy/supercritical-co2/). Increased efficiency means that for all forms of energy input (thermal/solar/nuclear/natural gas), the output in the form of power generation is increased when supercritical CO_2 is used as the working fluid over steam.

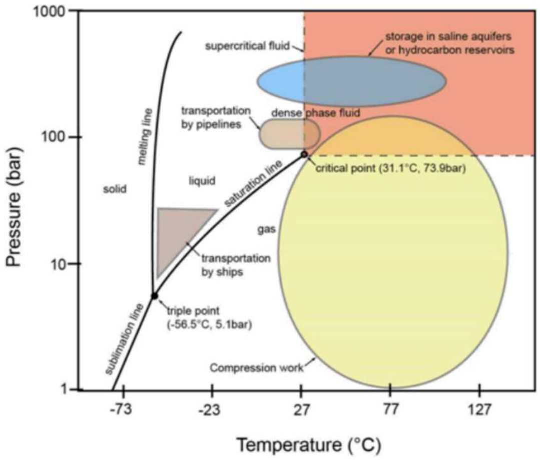


Figure 1: Various states in the CO_2 phase diagram showing the pressure and temperature domains

The development of super-critical CO_2 energy conversion systems requires a multi-materials approach that utilizes the most effective combination of materials to achieve safe, cost-effective construction and operation. The application-based selection of polymers finds common polymers such as Viton, polyetheretherketone (PEEK), ethylene propylene diene monomer (EPDM), ethylene propylene rubber (EPR) and polytetrafluorethylene (PTFE or Teflon) utilized in various extreme environments of sCO2 energy conversion systems. For example Viton, PEEK, EPR and Neoprene are used in pressure relief valves and pressure transducers. EPDM, EPR and Teflon are often used in turbomachinery (pressure boundary connections) and Nylon and PEEK are used in valve seats. Elevated temperatures (200-700°C) and pressures (4400-6000 psi) and combinations thereof, creep and fatigue conditions, corrosive environments due to moisture, pollutants from combustion products and impurities such as volatiles from polymers acting as contaminants and diluents in sCO2 are examples of various stress environments these polymers experience in energy conversion systems.

Most knowledge of polymer and monomer interactions with CO_2 was derived from the unique fact that super-critical carbon dioxide (sCO2) can be used as a solvent in many polymerization processes [1-4] due to its non-toxic, non-flammable and relative inertness. These applications have revealed a definite relationship between polymer microstructure and sCO2 effects. Polymer backbones with carbonyl groups, C-F bonds and double bonds show elevated CO_2 absorption. O-rings with these functionalities in their backbones (Viton, Kalrez, Teflon, and Silicone) showed the greatest loss of CO_2 from sealed fixtures [5]. It was found that polymers with greater flexibility of backbone, high free volume, lower glass transition temperature (Tg), and weak interactions between polymer segments such as in elastomers exhibited higher solubility in sCO2 over those that did not have the above microstructure [6]. On the other hand, since CO_2 is a weakly polar solvent, it cannot dissolve highly polar or hydrogen-bonded polymers such as poly (acrylic acid) [7]. High solubility and low diffusivity under prolonged conditions of exposure of these polymers to sCO2, as compared to N2, O2 or H2 gas behavior in the same type of polymers, leads to degradation mechanisms such as plasticization and lowering of polymer glass transition temperature [8]. CO_2 at weight concentrations of 8-10% can plasticize common glassy polymers with glass transition temperatures in the 8-100°C range to below room temperature [9]. These effects can be cumulative and are responsible for failure modes varying from slow leakages to formation of internal blisters, voids and cracks and consequent explosive rapid decompression (XRD) in the material. Long-term aging, swelling, plasticization, blister and crack formation can add up over service lifetimes and result in polymer failure leading to expensive repairs and down-times.

1.1. Common polymer failure modes seen in sCO2 systems

Of all failure mechanisms normally encountered with polymers in sCO2, explosive decompression seen in elastomers is the most destructive. Elastomers inherently contain voids and rigid inclusions that are produced during manufacture. Fluids or gases in contact with the material are absorbed and diffuse throughout the material. Explosive decompression, also called Rapid Gas Decompression (RGD, is normally caused by fast uncontrolled release of trapped gas in elastomers when positive high pressures are removed, and the part depressurizes (Figure 2).

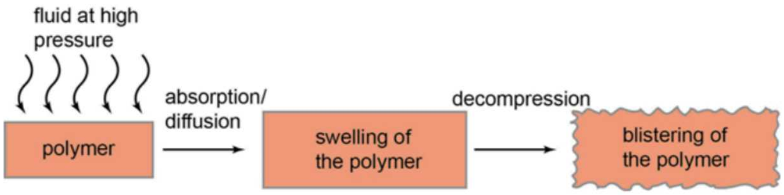


Figure 2. Pictorial depiction of explosive decompression phenomenon in polymers

(Courtesy: TWI-global website)

The material that is supersaturated with CO_2 releases the dissolved gas and this results in nucleation and growth of internal gas bubbles which forms surface blisters and eventually leads to can cause mechanical damage such as extrusion and blistering and eventual shredding of the elastomer (Figure 3).

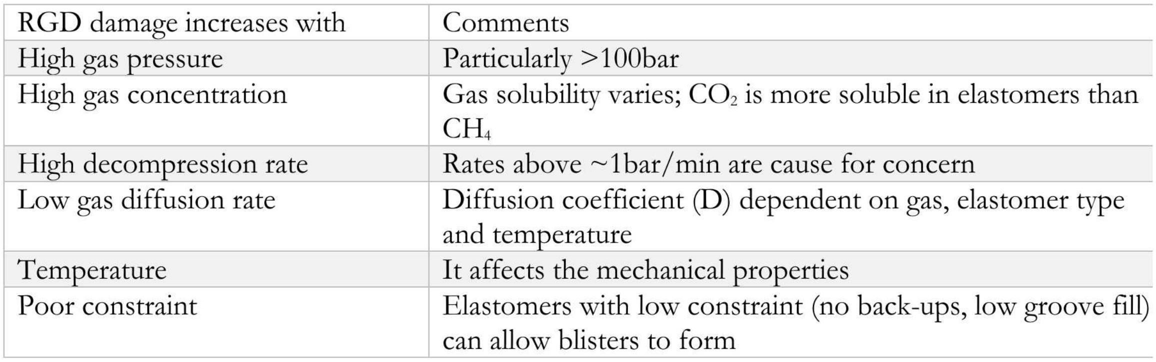
Figure 3. Examples of failures in elastomers in sCO2 service due to explosive decompression

The rate of depressurization plays a huge role in determining the extent of damage. Slow depressurization rates show less damage when compared to fast rates in polymers. This is a physical phenomenon. However, it is also influenced significantly by the permeation coefficients for super critical CO_2 transport through the polymers as well as affinity of the polymer for the gas. Table 1 shows the approximation of permeation coefficients and explosive decompression impact for different gases in common elastomers. The higher the solubility/diffusivity ratio, the greater the effect of explosive decompression. This ratio is highest for CO_2 amongst all the gases shown, which means that the polymers will exhibit maximum CO_2 effects over any other gas.

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

Table 1: Approximation of permeation, diffusion and solubility coefficients of various gases through common elastomers

Both physical and mechanical properties of polymers can be affected drastically by explosive decompression and plasticization effects when exposed to sCO2 under normal and extreme environments seen in energy conversion systems [10]. Table 2 lists some of the main factors that are responsible for the RGD phenomenon. Under benign operating conditions, polymers can be exposed to 1000 psia pressures during loop fill and saturation pressures during shut-down at room temperature. Extreme operating conditions such as in turbomachinery can accelerate explosive decompression with increase in pressures and temperatures. Elastomeric seals can be shredded in the process. Pressure and temperature cycling, transient exposure times, rapid pressurization and depressurization rates, and hydrostatic pressure effects combined with the compatibility of polymers with sCO2 under these conditions are critical factors towards defining material performance limits.



RGD damage increases with	Comments
High gas pressure	Particularly >100bar
High gas concentration	Gas solubility varies; CO_2 is more soluble in elastomers than CH_4
High decompression rate	Rates above ~1bar/min are cause for concern
Low gas diffusion rate	Diffusion coefficient (D) dependent on gas, elastomer type and temperature
Temperature	It affects the mechanical properties
Poor constraint	Elastomers with low constraint (no back-ups, low groove fill) can allow blisters to form

Table 2. Important factors that can affect Rapid Gas Decompression (RGD) in elastomers exposed to sCO2

Another major source of concern for polymers in sCO2 use is the effect of impurities such as SO_x and NO_x that can produce strong acids in the presence of water which can in turn catalyze hydrolysis [11]. Hydrolysis means depolymerization and release of leached molecules in the gas. If the smaller molecules do not leach out, the hydrolysis causes breakdown of the polymer and destroys its integrity and microstructure. Several measures can be adopted to prevent failure modes such as XRD and extend polymer lifetimes in sCO2 service. XRD can be prevented at manufacture-specified depressurization rates which are usually slow and gradual. However, these slow depressurization rates are not capable of accommodating transient conditions in sCO2 service such as emergency shut-downs and blow-downs. At low temperatures such as in blow-downs, elastomers become harder, less resilient and lose their memory. These require special XRD resistant O-rings as standard elastomers become hard and can no longer follow stem lateral movement. Polymers such as Teflon, nylon and stiffer polymers (80-90 durometer) are often used where appropriate [11]. Sometimes, design of the O-ring groove geometry and a high groove fill can also be used to help minimize XRD damage to elastomers. However, under extreme operating conditions, even design considerations can prove ineffective [12].

Figure 4. Failure seen with Viton O-ring due to SCO2 exposure

Elastomers such as neoprene and nitrile butadiene rubber (NBR or Buna N) used in seals and pressure relief valves and pressure transducers, are found to exhibit low absorption of sCO2. Numerous other elastomer XRD-resistant grades such as Aflas®, East-O-Lion 985® (HBNR) etc., are available depending on service, temperature etc. Typically, high hardness elastomers, with high filler loadings are used for these applications. Others such as Viton and PTFE are found to be unstable for the same applications (Figure 4). Therefore, in trunnion valves, nylon or PEEK back up rings are required immediately behind Viton O-ring. EPDM is a candidate that shows good promise in turbomachinery and VCO fittings in Coriolis meters. For extremely elevated temperatures (400°C) and pressures (4400 psi/30 MPa), elastomeric seals are replaced by PTFE-alloys which are spring-loaded with extremely fine surface finish for improved sealing [13].

A comprehensive literature survey pointed to the existence of critical knowledge gaps such as a lack of understanding of material performance limitations for common polymers used in sCO2 systems. Significant amount of testing of polymers in sCO2 has been conducted in lower pressures (1000-1800 psig), lower autoclave velocities and slightly-above room temperature (55-60°C) conditions. This does not mimic the conditions that these materials will see in actual power cycles. This study involves a baseline investigation on compatibility of polymers in sCO2 to study the effects of lower temperatures (60°C-150°C range), and pressures (2000-5000 psig/14-35 MPa) at typical flow rates (0.06kg/hour). Sandia National Laboratories (SNL), CA partnered with University of Wisconsin to conduct these experiments with exposures of polymers performed at the University of Wisconsin and characterization and data analyses by SNL, CA.

2. EXPERIMENTAL PROCEDURE

2.1 Test Conditions

Two tests were designed: one was exposure at 150ºC and a second one at 100ºC. The 150ºC test involved the use of a 14” 2-161 FF202 (Durometer = 90) O-ring from Parker and a 13” 2-161 EPDM (durometer = 90) O-ring from Precision Rings. The 100ºC test included nine 1and 3/8” off-the-shelf polymer O-rings requested from McMaster Carr (Buna N, EPDM, Neoprene, PTFE, EPR, Nylon, PEEK, Viton and FF 202) (Table 3 below). Super critical CO2 pressure in the test autoclave was maintained at 20MPa with a flow rate of 0.06 kg/hour.

Polymer type	Temperature (°C)	Pressure (MPa)	Time (hours)
Perfluoroelastomer FF202-90	150	20	1000*
Ethylene Propylene diene monomer EPDM			

Perfluoroelastomer FF202-90	100	20	1000*
Ethylene Propylene diene monomer EPDM			
Buna N (Nitrile Rubber)			
Neoprene (Polychloroprene)			
Teflon (Polytetrafluoroethylene)			
Viton (FKM)			
Ethylene Propylene Rubber (EPR)			
Nylon (Polyamide)			
PEEK (Polyetheretherketone)			

*= samples were withdrawn at two intervals (t = 200 hours and t = 1000 hours) and compared to t = 0 hours (control) for changes

Table 3. Details of 150°C experiment (top) and 100°C experiment(bottom)

2.2 Polymer characterization

All polymers for the two tests were characterized for physical and chemical properties prior to sCO2 exposure. After removal at t=200 hours and t=1000 hours, the O-rings were characterized for the same properties for changes that could indicate polymer erosion, solubility or degradation in sCO2 environments for the test conditions. Table 4 below shows a comprehensive description of polymer properties and appropriate characterization methods used in this study.

Polymer property	Characterization technique
Density	ASTM D 792 (Archimedes principle)
Mass	Gravimetric measurements with lab scale with ±0.1 mg sensitivity
Glass transition temperature (T_g) and modulus changes	Dynamic Mechanical Thermal Analysis (DMTA)
Molecular and structural changes	ATR-Fourier Transform Infra-Red Spectroscopy (ATR-FTIR)
Texturing and surface damage	Optical Microscopy
Compression set	(ASTM D395 Method B)
Internal voids and damage	Micro Computerized Tomography (Micro-CT)

Table 4. Polymer characterization and relation to physical/chemical effects

Density of the exposed and non-exposed specimens was measured following ASTM D 792. Sample densities and masses were measured immediately after removal from the autoclave as well as more than 48 hours later. Density was measured with the goal of checking for absorption and retention of sCO2 that can cause swelling in polymers and mass was measured for loss of volatiles from the polymer during depressurization. Dynamic mechanical thermal analysis is a characterization method commonly used to study the viscoelastic nature of polymer in which a sinusoidal stress is applied and the strain in the material is measured as changes in storage and loss moduli. The temperature of the sample is varied such that the variations in the modulus can be used to pinpoint the glass transition temperatures of the material. In the context of this study, sCO2 can change the glass transition temperature (T_g) as well as the storage modulus of the polymer.

ATR-FTIR (Attenuated FTIR) can measure the chemical interaction of sCO2 leading to permanent molecular changes that manifest in the spectra as peak loss, peak shifts or new peaks. It is important to generate the spectra of the polymers prior to exposure for comparison. Surface damage and texturing was studied using optical microscopy at high magnifications. Internal voids and cracks because of rapid rates of depressurization were better characterized using micro-CT method. Compression set was measured using ASTM D 395 Method B wherein the specimen is compressed to 75% of its original height over a set time and temperature which is used to calculate permanent deformation of the polymer after exposure. In our study, if the polymer has undergone chemical changes in the form of loss of crosslinking and become “soft”, it would manifest itself as a large compression set.

3. RESULTS And DISCUSSION

Polymer characterization data before and after exposure to sCO2 was used to understand physical and chemical effects produced in polymers due to the high diffusivity and solubility, and low polarity of SCO2 in these systems. Physical effects in the polymers range from change in modulus/strength to surface or internal voids and cracks due to rapid depressurization. Chemical effects range from change in molecular structure, plasticization of matrix and therefore drop in glass transition temperature and increased deformation due to the polymers becoming soft after exposure such that they undergo permanent deformation in the compression set test. The molecular structures of the nine polymers are as shown below (Figure 5) and will be used to explain the physical and chemical effects observed with sCO2 exposure.

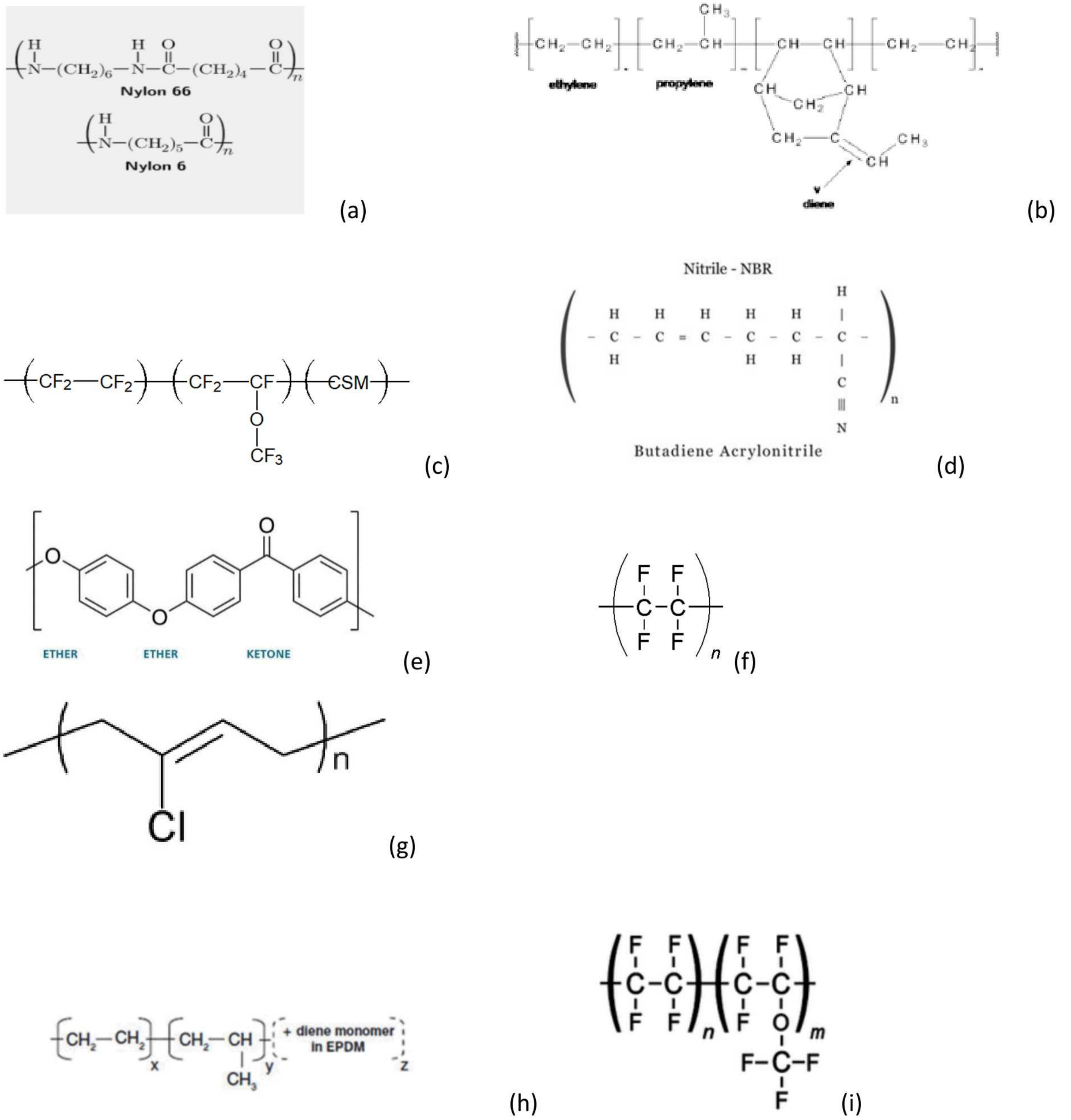


Figure 5. Molecular structures of (a) Nylon 6,6 (b) EPDM rubber (c)Perfluoroelastomer (d) Nitrile rubber (e) PEEK (f)PTFE (g) Neoprene (i) Viton A

3.1 Density changes

For all nine polymers exposed to sCO2 at the different temperatures (150°C and 100°C), except for EPR at 100°C, density either increased or decreased after sCO2 exposure. EPR tested at 100°C showed no change in density. EPDM, which is similar in molecular structure to EPR showed 4% change in density at 150°C and almost no change at 100°C. This molecular structure, therefore, maybe conducive to not swelling under sCO2 pressure. The non-polar nature of the polymers as opposed to the polar nature of sCO2 does not permit easy diffusion of the latter. FF202 at 150°C showed only a small change in density whereas the same polymer at 100°C in sCO2 showed a decrease in density because of sCO2 absorption and increased even more later. The perfluoroelastomer is highly polar due to the presence of the large fluorine atoms on the backbone and the permeation of sCO2 through this polymer is slow despite the match in polarity. PTFE and Viton are polymers which showed similar tendencies to decrease densities with exposure time. They swell in sCO2 in the first 200 hours at 100°C and continue to pick up sCO2 slowly with time. The diffusion of sCO2 through these polymers is very slow due to the bulky fluorine atoms on the polymer backbones.

Nylon 6,6, PEEK, Neoprene, Buna N all showed increasing densities with time. The presence of the polar C=0 group on the backbones of Nylon, and PEEK, the presence of the polar Cl atom on the backbone of Neoprene and the -C-N group on Buna N (Figure 5) should show affinity for sCO2 and hence these polymers show increased densities due to increased diffusion and solubility of sCO2.

From Figure 7 below, the largest change in densities is for Neoprene and Buna N followed by Nylon and PEEK. PTFE, Viton and FF202 show similar low-to-medium changes in density and EPR and EPDM are the most resistant to sCO2 exposure for density changes. The polar natures of the polymers and the functional groups on their backbones are instrumental in increased diffusivity and solubility of sCO2 in the polymer matrix causing large density changes. This can result in the seal losing its ability to seal upon exposure and over time and many numbers of sCO2 cycles, be susceptible to explosive decompression phenomena. EPR and EPDM are non-polar and less susceptible to density changes with exposure.

3.2 Mass changes

Mass changes in polymers are measured with the goal of checking to see if they tend to retain sCO2 even after removal from the test due to high solubility of the latter in the polymer. It is also a measure of the possible loss of volatiles from these polymers during the process of depressurization. Loss of plasticizers as a volatile can cause the polymer to lose its elasticity with time and result in a loss of sealing ability. Mass and density are related properties. If the polymer shows a decrease in density and loses mass, it will swell in sCO2 and lose volatiles at the same time.

For FF202 at 150°C and 100°C, the change in density and mass was insignificant (Figure 8). This polymer is resistant to sCO2 at both temperatures. For EPDM at 150°C, density decreased by 4% and mass decreased by 16%. For the same polymer at 100°C, there was no significant mass loss at all. The EPDM mass loss is, therefore, related to temperature and the polymer loses more mass/volatiles as use/test temperature goes up.

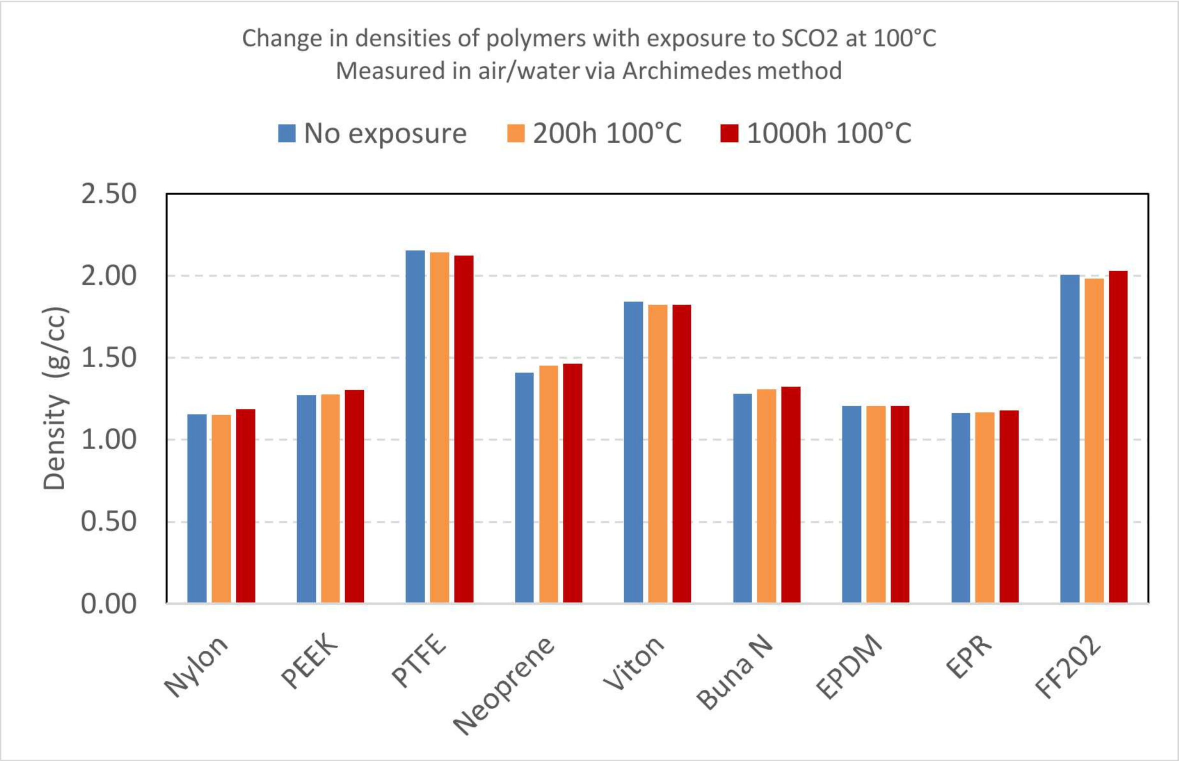


Figure 6. Change in density with exposure to sCO2 at 100°C for polymers shown

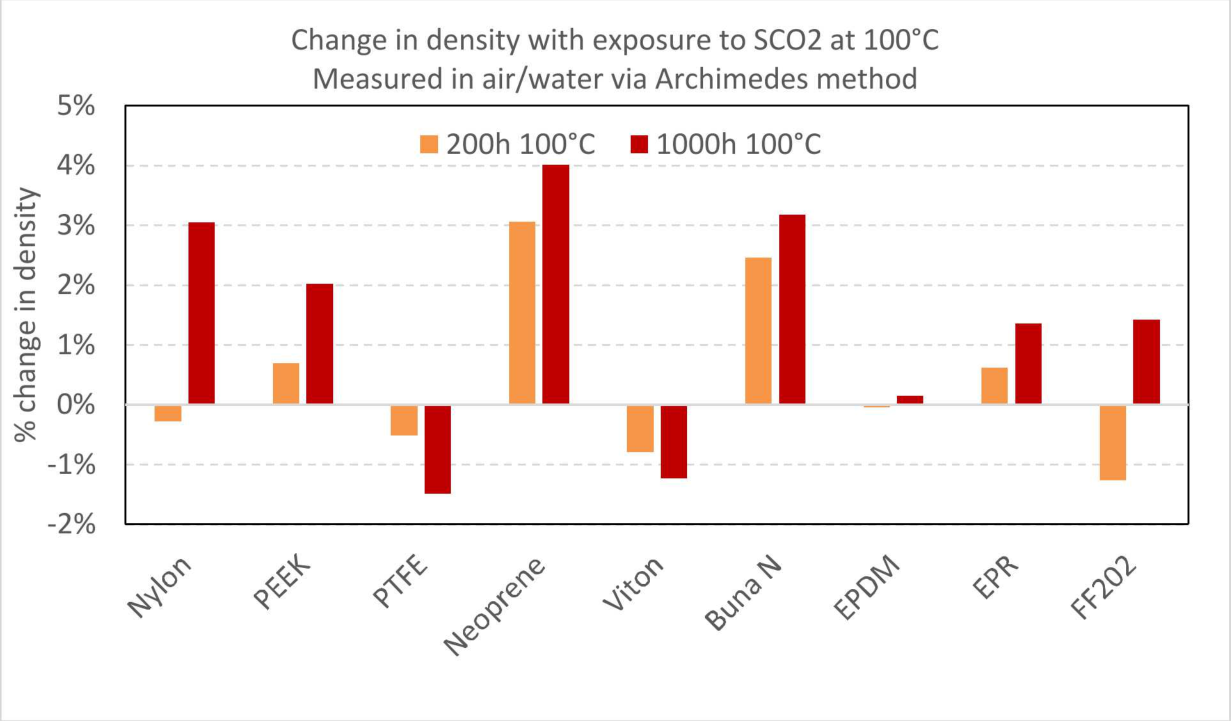


Figure 7. Percent change in density for polymers shown upon sCO2 exposure at 100°C

For Viton, PTFE, Nylon, PEEK and FF202 do not show significant changes in mass at 100°C which means no significant loss of volatiles (less than ±2%) (Figure 9). Neoprene, Buna N show large decreasing mass and increasing density with time which could mean that SCO2 diffusion is encouraged by polar groups present on backbone and that loss of volatiles with SCO2 diffusion is a possibility. EPR shows an increase (about 4%) and the mechanism of interaction with SCO2 may be slightly different from EPDM because EPDM has polar double bonds in its molecular structure and EPR has none.

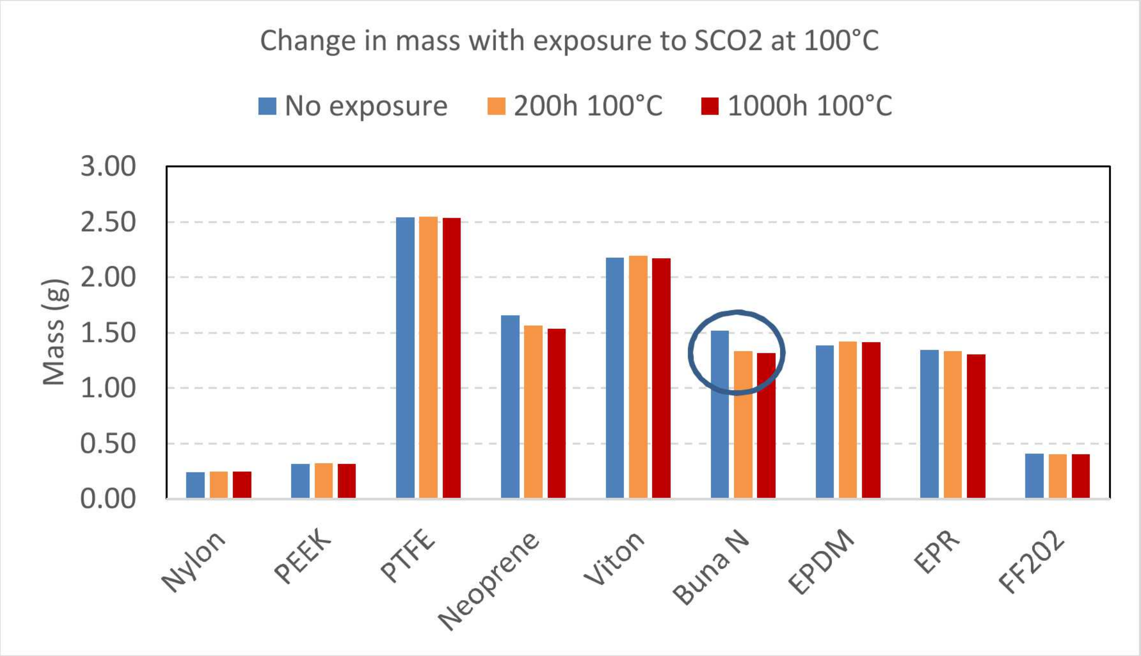
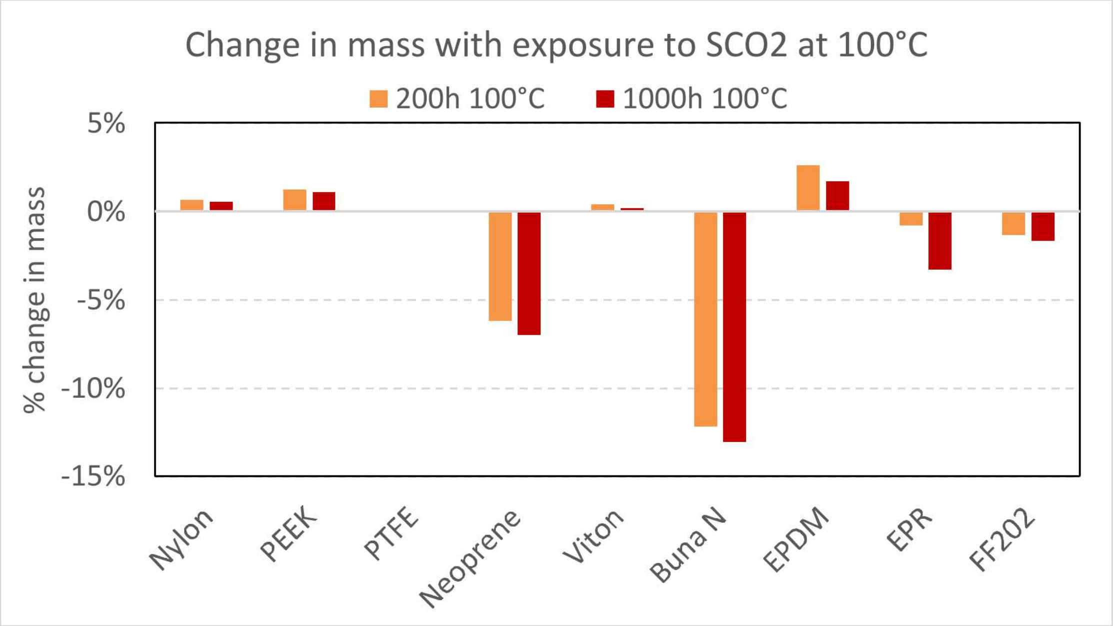


Figure 8. Change in mass with exposure to sCO2 at 100°C for polymers shown (top) and percent change in mass with sCO2 exposure at 100°C for the same polymers (bottom)



3.3 Complex moduli and glass transition temperature changes

Dynamic mechanical thermal analyses of polymers before and after sCO2 exposures indicated some interesting trends for changes in complex moduli (storage and loss) and glass transition temperatures (T_g). The viscoelastic natures of the polymers respond to sCO2 exposure and show interesting trends with times of exposure. For example, for FF202 polymer, storage modulus (indicative of the elastic nature of the material) tends to increase significantly (63%) upon 200 hours of sCO2 exposure and then falls back to almost to that for the unexposed polymer at 1000 hours (Figure 9). The glass transition temperature shows a tendency to increase from that of unexposed polymer to 1000 hours. The initial increase in modulus can be the result of temperature-aided migration of 20 MPa sC02 pressure at 150°C. This polymer has large fluorine atoms on the backbone and does not permit diffusion of sCO2 into the free volume easily. However, the high temperature causes the softening of the polymer permitting some movement of polymer chains that aids diffusion of sCO2 with time into the polymer. Upon equilibration in sCO2 with time, this temporary balancing effect is gone. The sCO2 has now fully migrated into the free volume slowly and polymer is restored to almost the original modulus. This change in modulus is accompanied by a substantial 75% increase in T_g indicating that it possible that the polar sCO2 binds to the fluorine substituted backbone with weak intra molecular forces (Vander Waal type forces) for prolonged exposure times.

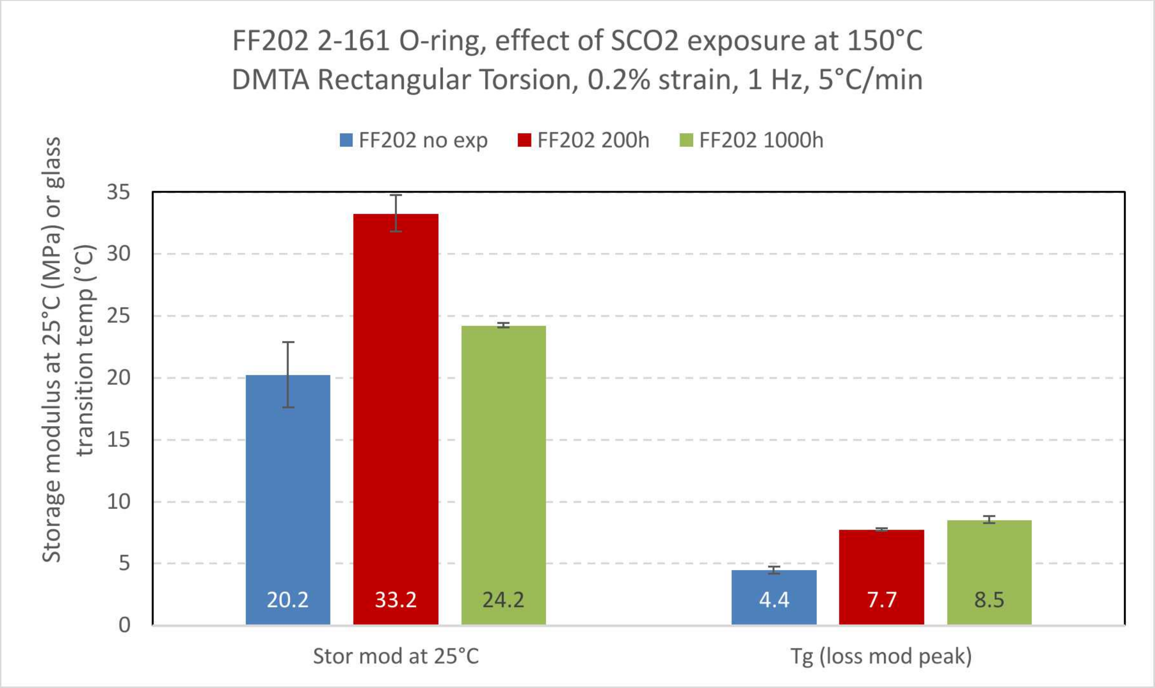


Figure 9. Storage modulus of FF202 polymer before and after sCO2 exposure at 150°C

For EPDM at 150°C, the storage modulus increases by 114% and then again, like FF202, drops back to almost original modulus values. This increase in modulus could be due to same hydrostatic-temperature effect seen with FF202 at 200 hours that slowly disappears as the polymer saturates with sCO2. For EPDM, however, the glass transition temperature is steady and does not change much indicating very little interaction of this polymer (due to its non-polar nature) with sCO2 (Figure 10).

For the same polymers at 100°C, the trends were slightly different. FF 202 did not show any increase in storage modulus with time of exposure (Figure 11); but the glass transition temperature increased steadily with time of exposure as it did at 150°C. This behavior shows that the transport of sCO2 in FF202 is temperature-controlled. At higher temperatures, the storage modulus changed significantly because elevated temperature aided the transport of the sCO2 into the polymer. At 100°C, the molecular structure of the polymer (with large fluorine atoms that block sCO2 migration) is dominant and diffusion is extremely slow. The $T_{g,}$ however, continues to increase like before because of possible weak interactions between the migrating sCO2 molecules and the polar fluorine atoms.

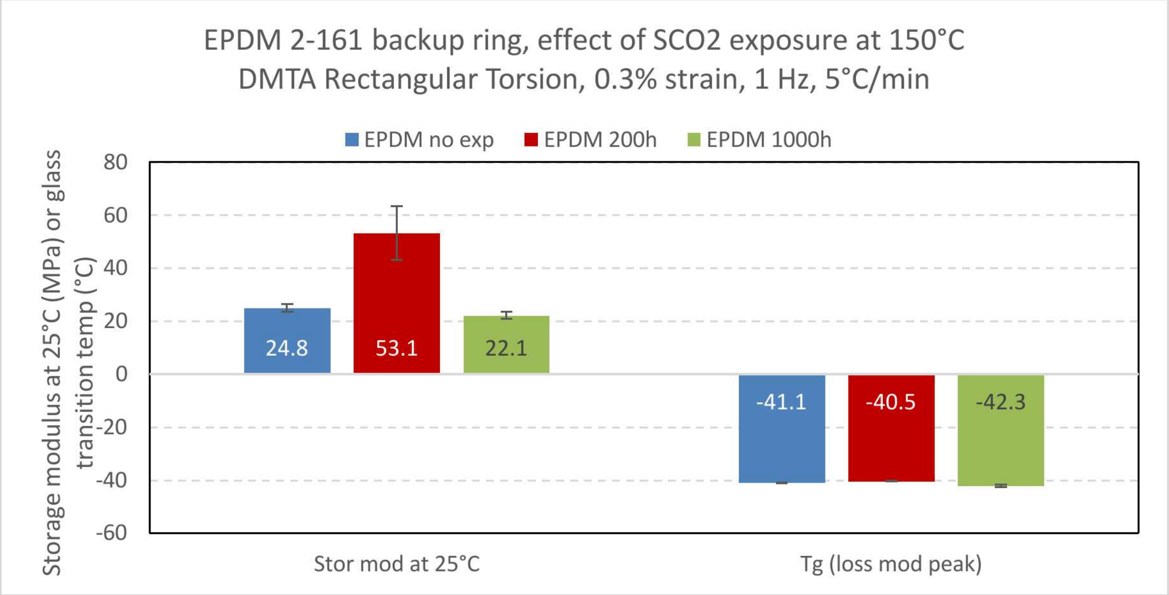


Figure 10. Storage modulus and T_g of EPDM polymer before and after sCO2 exposure at 150°C

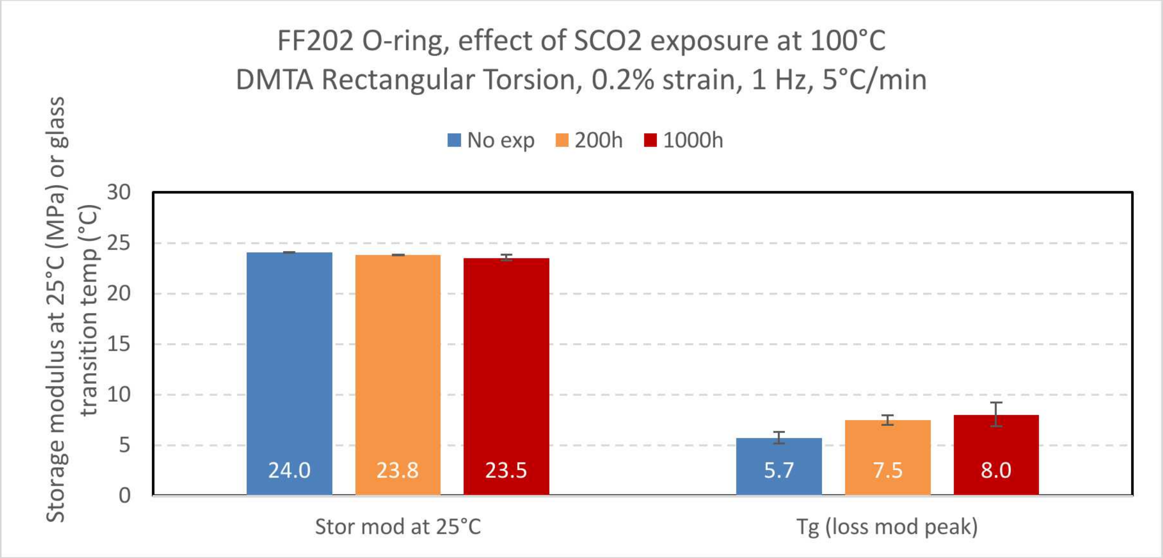


Figure 11. Storage modulus and T_g of FF202 before and after sCO2 exposure at 100°C

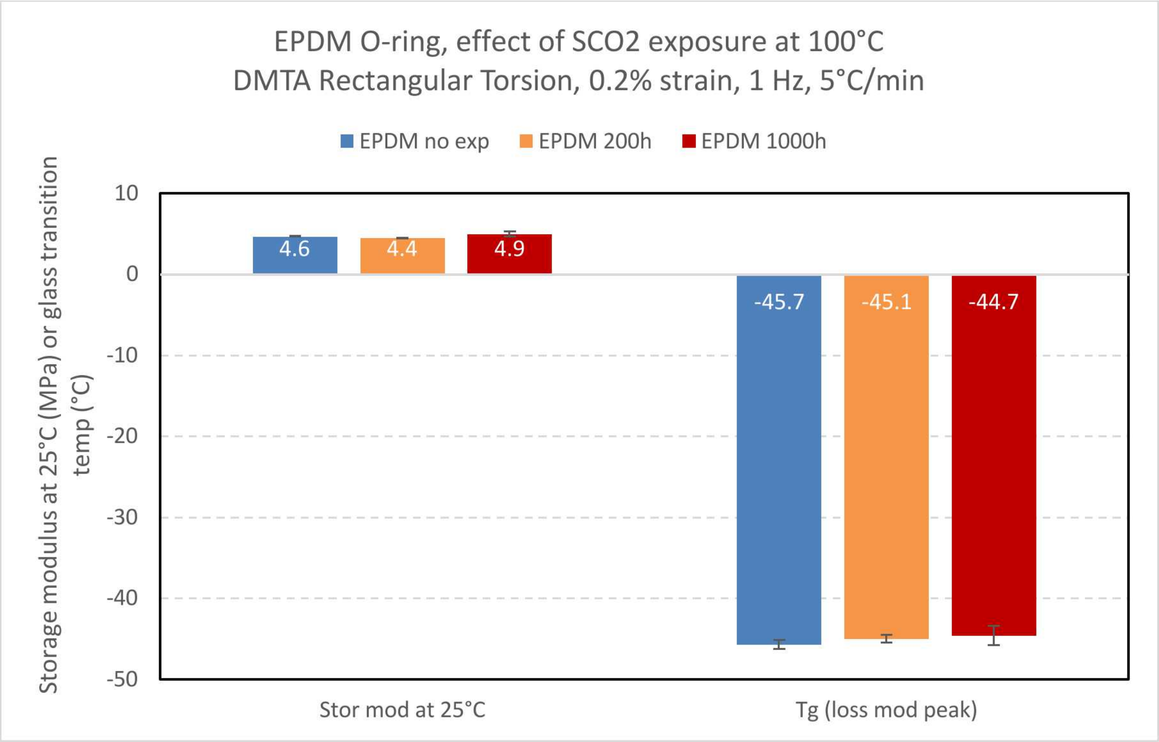


Figure 12. Storage modulus and T_g of EPDM before and after sCO2 exposure at 100°C

Like FF202, the dramatic increase in storage modulus at 200 hours at 150°C is not seen for EPDM for the same exposure at 100°C (Figure 12). It seems that the diffusion of sCO2 in EPDM is also temperature-controlled and is not as fast at 100°C as it is at 150°C. As with 150°C, the interaction of this polymer with sCO2 at 100°C is minimal and hence the Tg is not influenced very much.

For Buna N, the exposure to sCO2 at 100°C shows a dramatic increase in storage modulus and glass transition temperature with time (Figure 13). At t=200 hours, the modulus is six times that of the unexposed polymer and at t=1000 hours, it is 12 times greater. The glass transition temperature increases by 66% as time of exposure increases. Buna N has strong -C-N functional groups as side chains and double bonds present on the main backbone. These polar groups/high electron density bonds can possibly develop weak Vander Waal's type interaction with the migrating sCO2 binding it into the free volume spaces. This could be the reason for the increasing storage modulus and glass transition temperature with time of exposure to SCO2 at 100°C. Since this polymer was not tested at 150°C, it is not possible to determine its behavior at 150°C. It can be predicted, however, that with higher temperature, the rate of diffusion would be greater and these SCO2 interactions would increase.

PEEK, Nylon and PTFE are three thermoplastics that show similar trends in sCO2 exposure. PEEK has the highest storage modulus followed by Nylon and then PTFE. The moduli of these polymers do not change much with increased exposure times at 100°C. PEEK shows a slight increase in storage modulus (Figure 14) as time of exposure increases which may be due to the interaction of the -C=O groups with sCO2. The highly aromatic "ladder" structure of PEEK must hinder the approach of sCO2 while polar interactions continue. Its Tg decreases slightly possibly due to matrix plasticization effects.

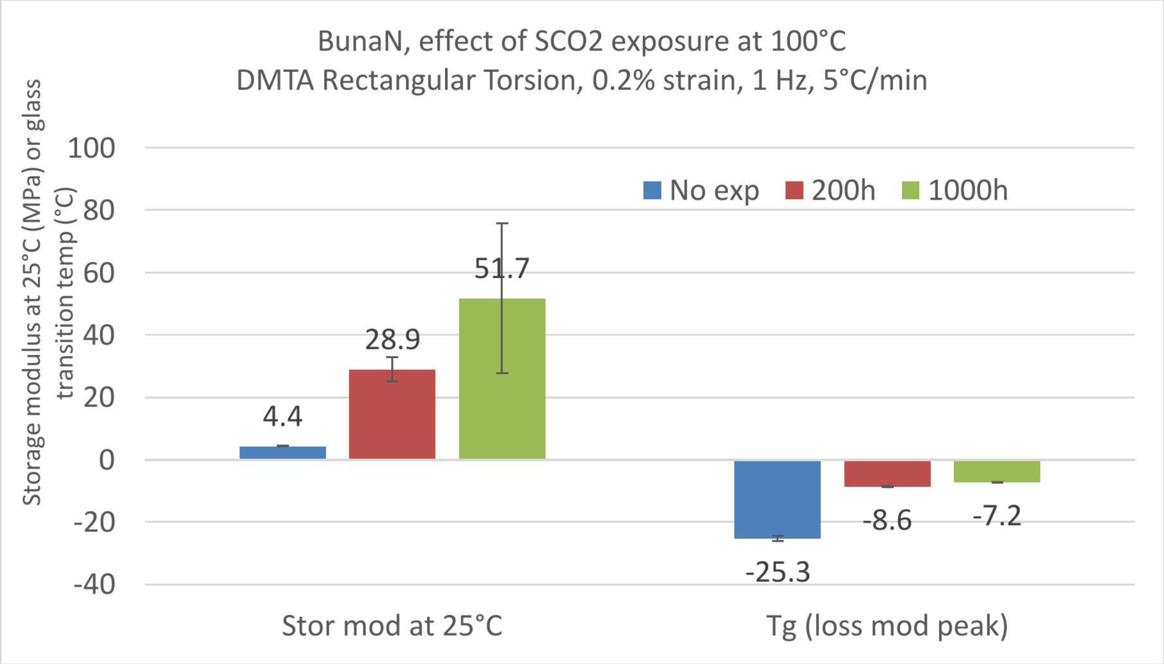


Figure 13. Behavior of Buna N in sCO2 for 1000 hours of exposure at 100°C

With Nylon, the storage modulus drops a little at t=200 hours and then stabilizes at a slightly higher value at 1000 hours while the Tg does not change much (Figure 15). The same -C=O interaction seen with PEEK and sCO2 is possible in Nylon. The structure of Nylon is more linear and sCO2 approach is much easier than with PEEK thereby causing a drop in the storage modulus. Since the Tg does not change much, this interaction is minimal and does not seem to result in plasticization for 1000 hours at 100°C.

PTFE shows the same tendency to increase modulus as PEEK (Figure 16). Just like with the FF202, the large fluorine atoms on the PTFE polymer backbone can hinder sCO2 approach sufficiently and make it slow enough for positive weak interactions between the fluorine atoms and sCO2 to be possible at 100°C. There are two glass transition temperatures seen with PTFE because it is usually a bimodal mixture of molecular weights. These do not change much indicating that the plasticization at 100°C is not a concern for this polymer with sCO2 exposure.

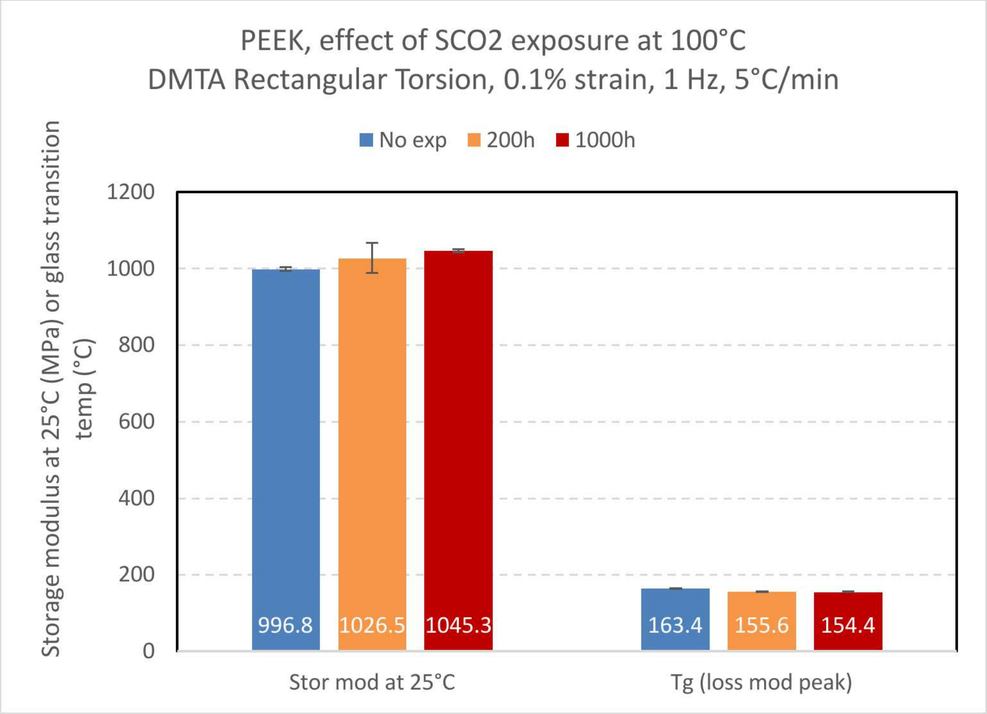


Figure 14. Behavior of PEEK in sCO2 for 1000 hours of exposure at 100°C

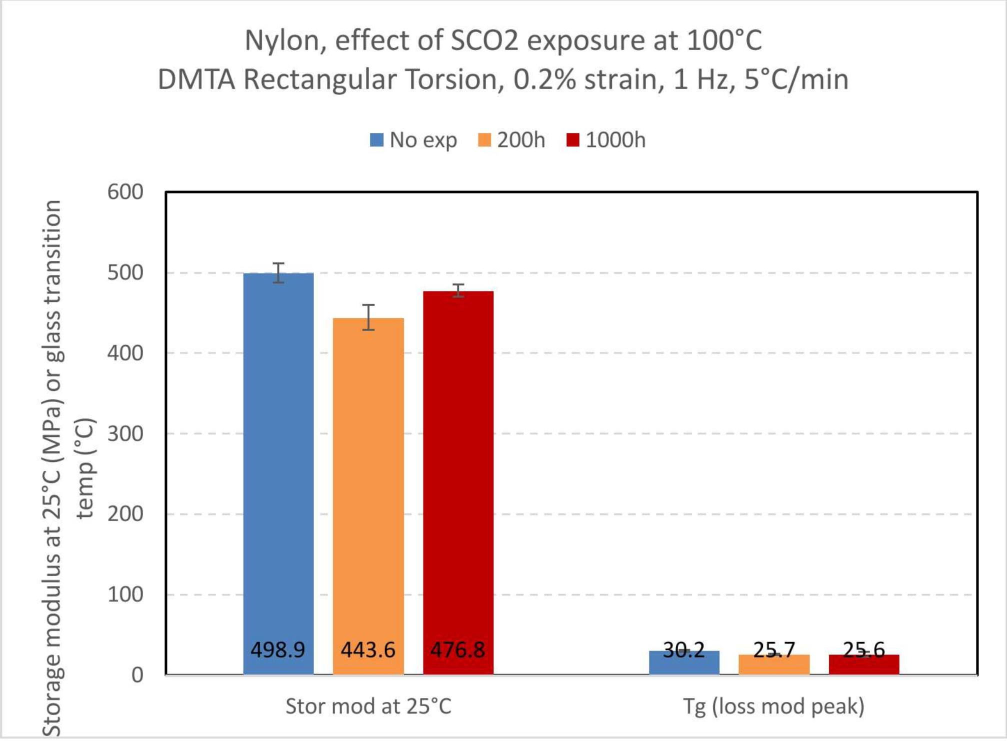


Figure 15. Behavior of Nylon in sCO2 for 1000 hours of exposure at 100°C

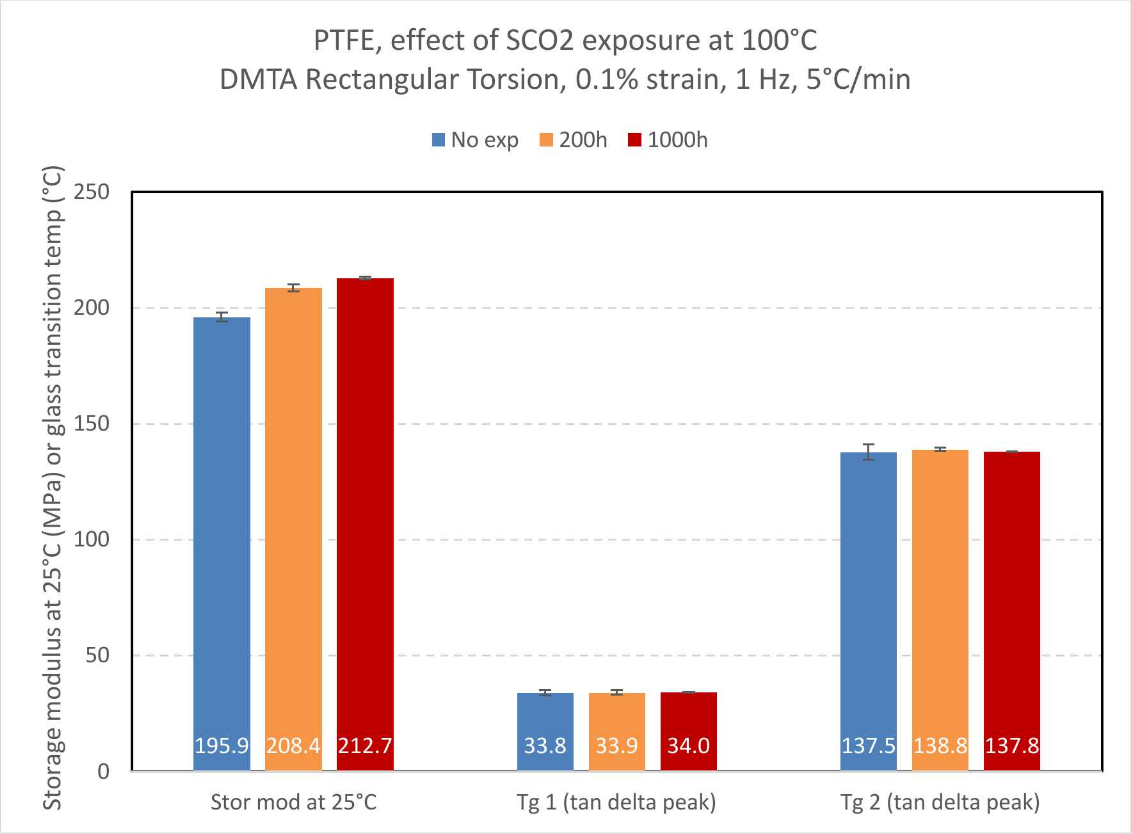


Figure 16. Behavior of PTFE in sCO2 for 1000 hours of exposure at 100°C

Viton is a fluoroelastomer used widely for seal applications in sCO2. Its high temperature resistance and high chemical resistance play a critical role in sCO2 energy conversion systems. Figure 17 shows very little change in storage modulus with times of exposure at 100°C for this polymer. Its molecular structure permits interaction with the polar sCO2. However, like the FF202, the large fluorine atoms do not permit easy diffusion through the chains at 100°C. The Tg drops very slightly due to plasticization effects.

For EPR, the molecular structure resembles that of EPDM without the diene monomer and like the latter, the interaction of sCO2 with the non-polar EPR is minimal. However, the storage modulus increases dramatically with time and becomes 2 times the unexposed value at 1000 hours of exposure at 100°C (Figure 18). This behavior is unusual and cannot be explained based on polarity. The change is Tg is minimal as one would expect for little interaction with sCO2.

The polymer structure of Neoprene resembles that of Buna N with double bonds in the backbone and a pendant polar (Cl for Neoprene and -CN for Buna N) functionality (Figure 5). The behavior of this polymer in sCO2 at 100°C resembles that of Buna N with a dramatic increase in storage modulus with time of exposure. The modulus goes up to 2.5 times that of the unexposed at t=200 hours and about 4 times that of unexposed at t=1000 hours (Figure 18). The Tg does not change significantly for this exposure. Molecular structure indicates that there is a possible polar-polar interaction between the pendant Cl moiety and sCO2 such that an increase in storage modulus is seen.

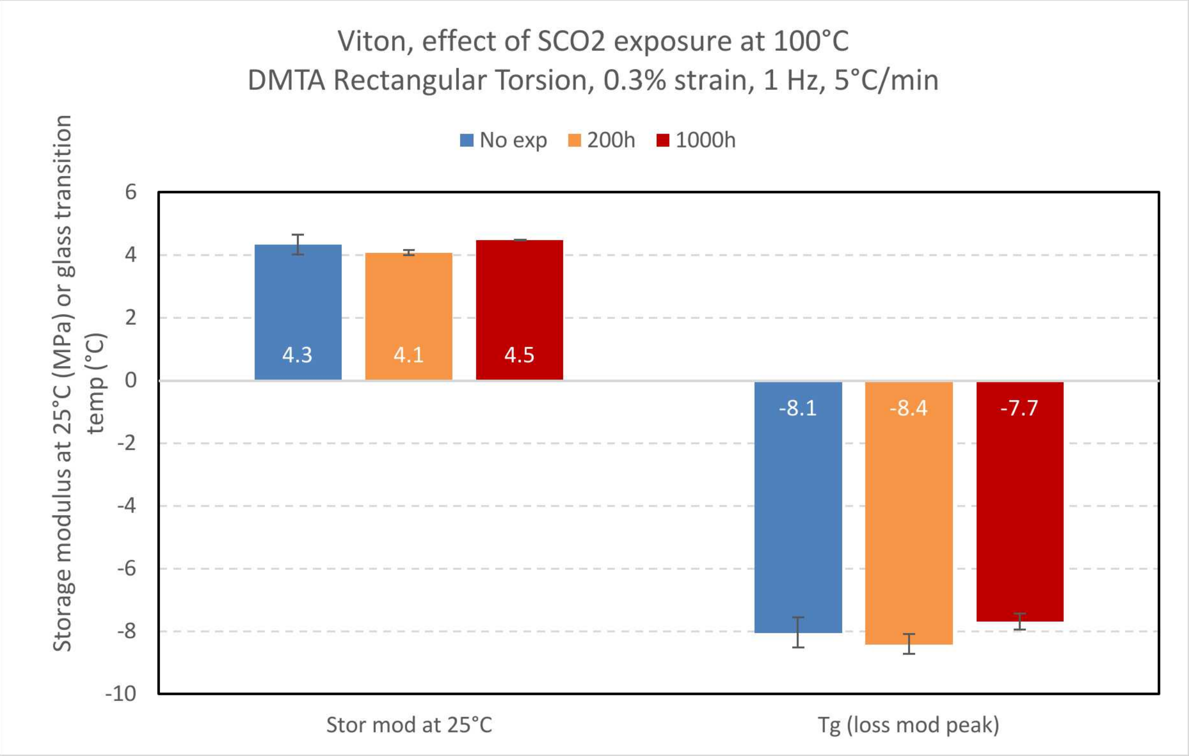


Figure 17. Behavior of Viton in sCO2 for 1000 hours of exposure at 100°C

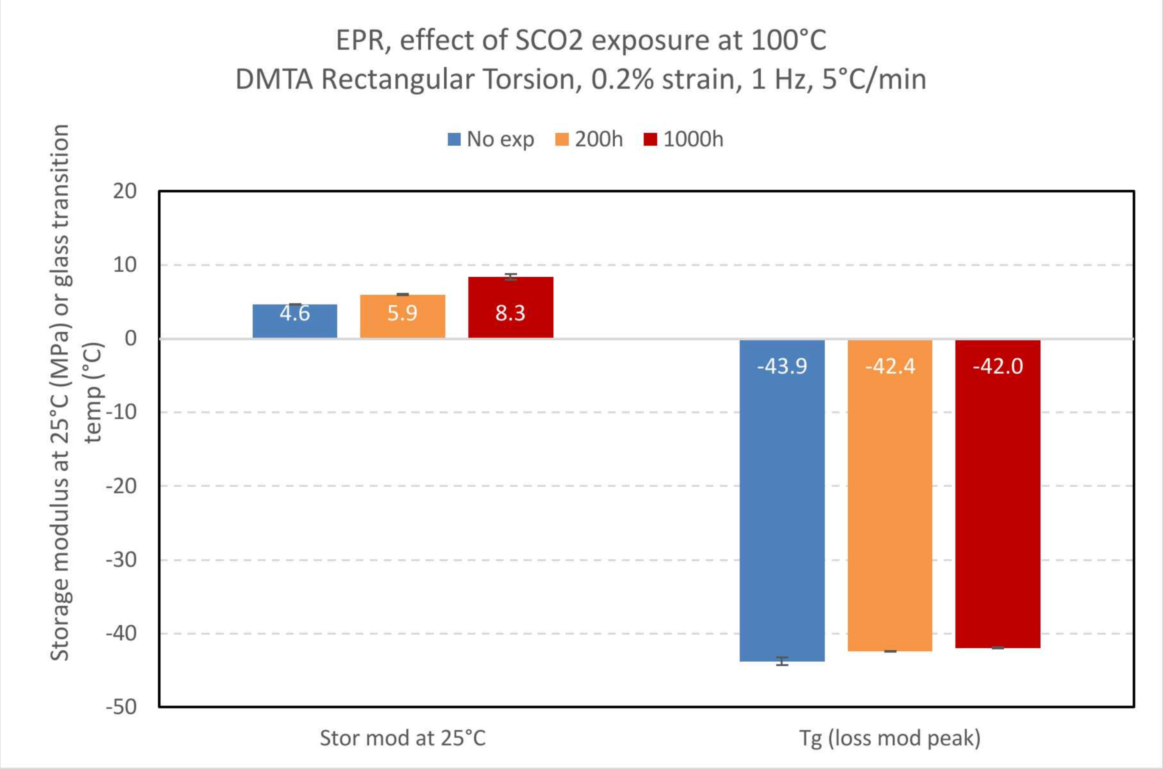


Figure 18. Behavior of EPR in sCO2 for 1000 hours of exposure at 100°C

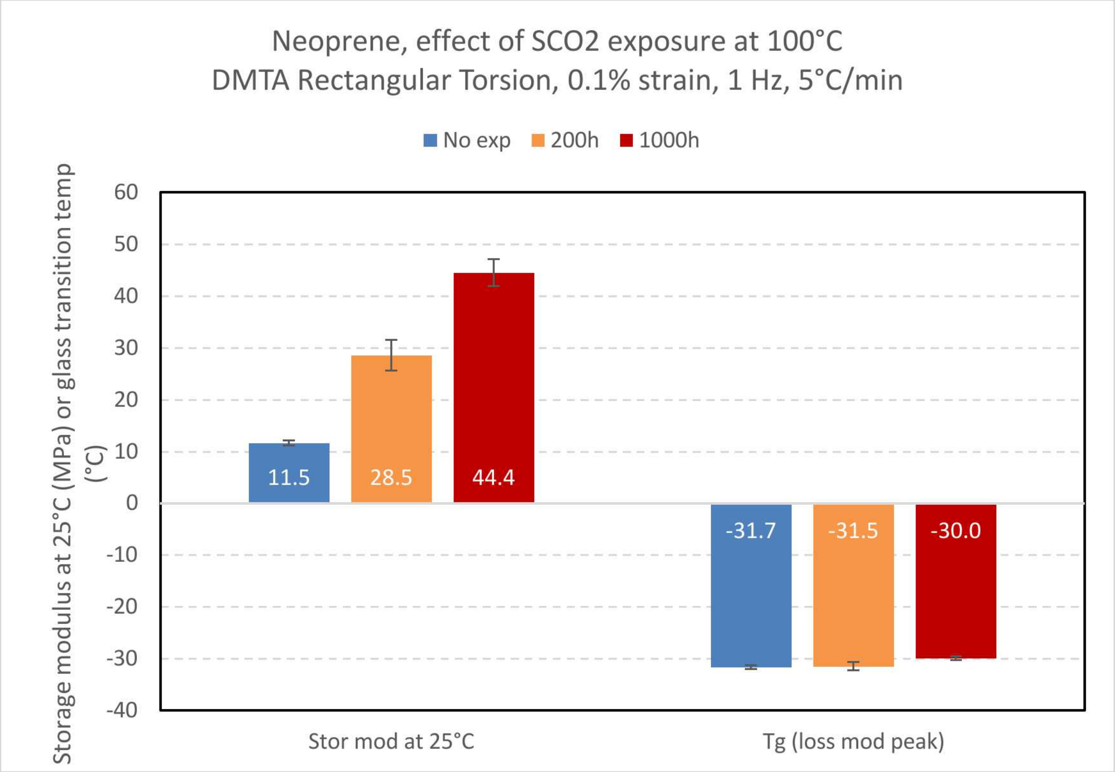


Figure 19. Behavior of Neoprene in sCO2 for 1000 hours of exposure at 100°C

3.4 Compression set data for polymers in sCO2

Compression set for a polymer is a measure of its capability to permanently deform when a set load is applied for a certain length of time at a certain given temperature. A high compression set number is undesirable because it indicates the polymer's susceptibility to being deformed such that it is incapable of proper sealing. When rubbers are saturated with sCO2, they tend to be softer due to a plasticization effect of the polymer matrix. This softening effect can cause the compression set of the polymer to be higher after exposure than before.

Figure 20 compares the compression set for FF202 and EPDM for sCO2 exposure at 150°C. For FF202 there is a massive increase (more than 3X the unexposed value) in compression set from t=0 to t=200 to t=1000 hours. This could indicate more solubility due to polar interactions of F and SCO2 in SCO2 allowing more penetration by SCO2 making the polymer softer and more deformable. Some recovery happens when SCO2 diffuses out of the polymer at 1000 hours. For EPDM, there is a 55% increase from t=o to t=200 hours and then at t=1000 hours, the compression set triples the from original value. This trend could indicate slow diffusion of SCO2 int EPDM due to non-polarity of the polymer and lack of interaction with SCO2. With prolonged time, more diffusion of SCO2 happens and softens the polymer thereby increasing the compression set considerably. FF-202 changes in compression set at t=0 than EPDM which could be the effect of polar vs non-polar nature of the two polymers.

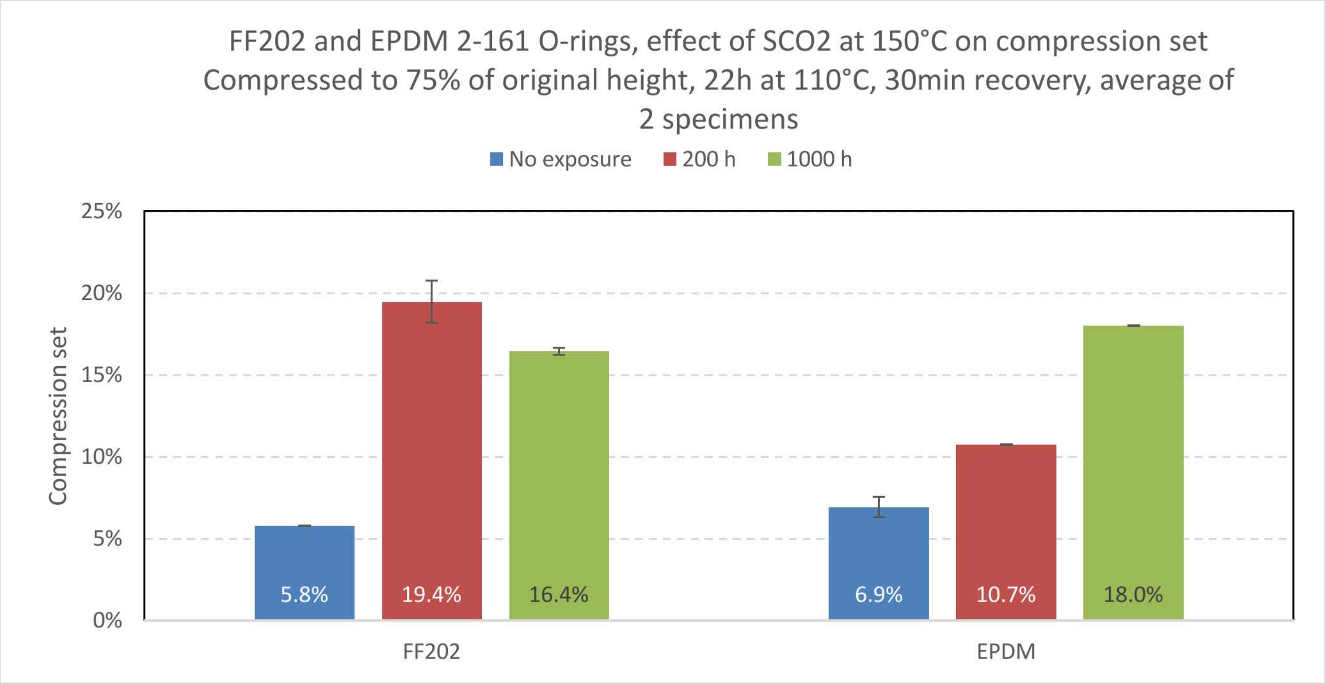


Figure 20. Compression set for FF202 and EPDM rubbers before and after sCO2 exposure at 150°C

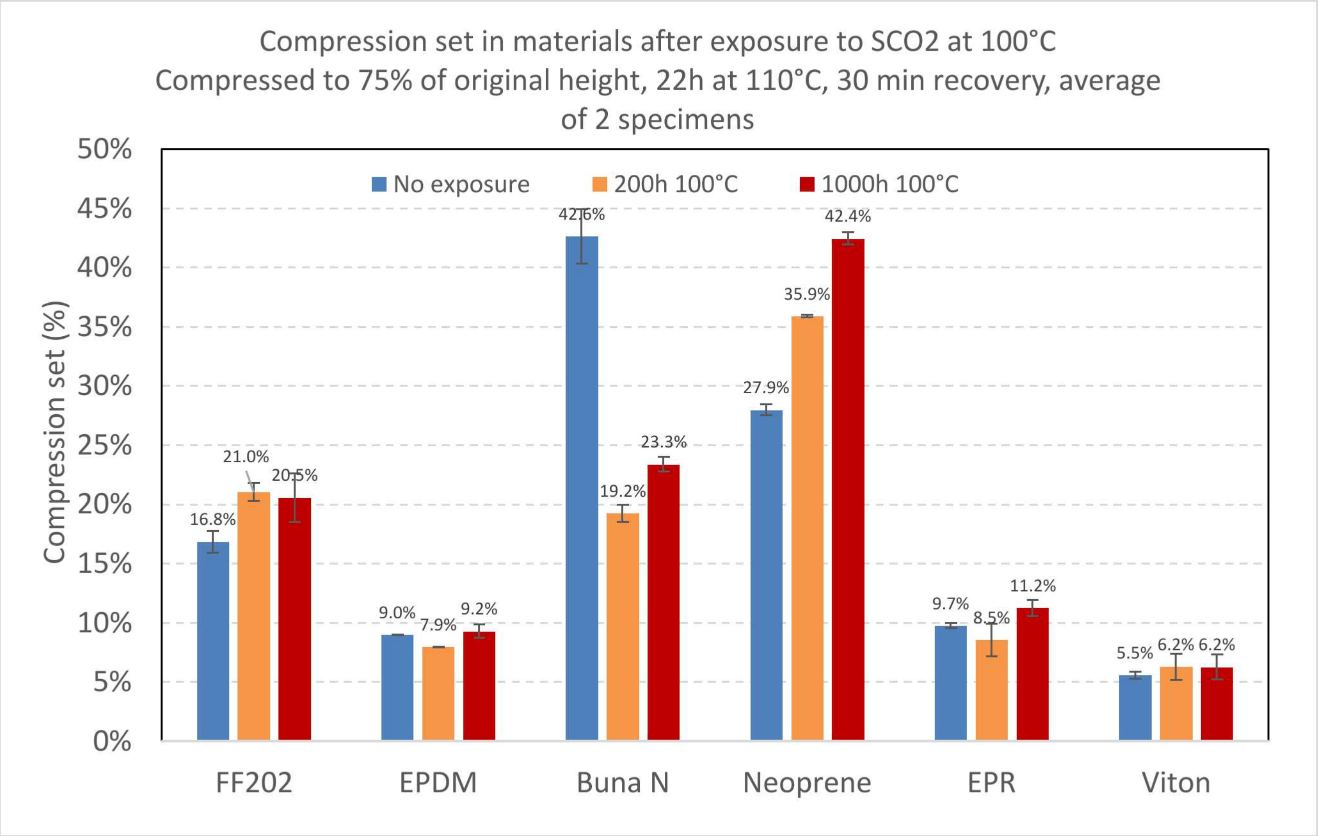


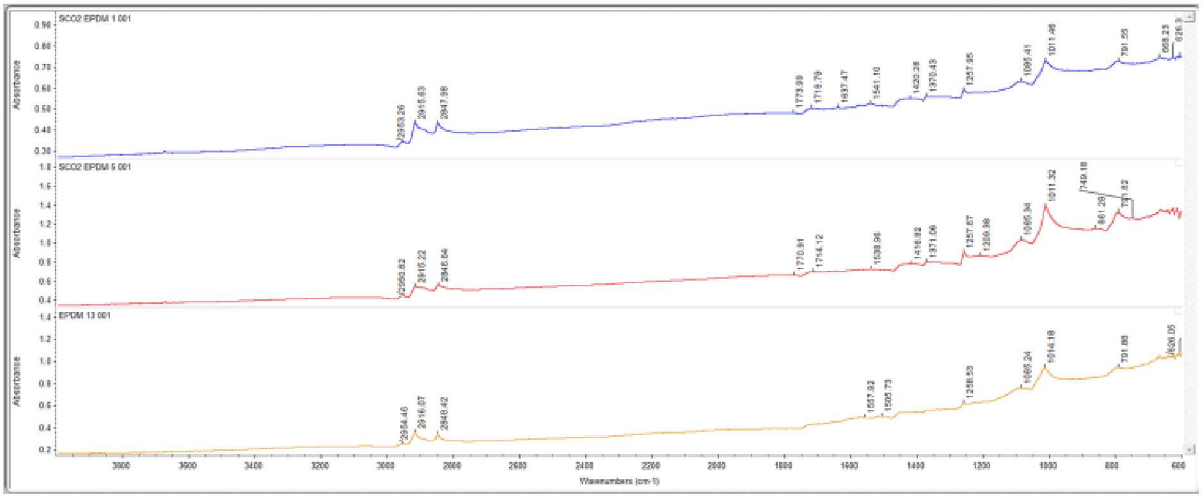
Figure 21. Compression set values for polymers before and after sCO2 exposure at 100°C

Following similar trends in other polymers in this study, compression set only changes slightly for fluorinated elastomers such as FF202 and Viton at 100°C. Overall, Viton has much lower compression set compared to FF202. sCO2 interaction in these polymers is like each other given the similarities in their molecular structure. EPDM and EPR show similar compression set numbers at around 9-10%. The trend seen for t=200 hours and t=1000 hours for both polymers is that there is no significant increase with time of exposure at 100°C. These polymers are non-polar and do not interact with sCO2. Buna N and Neoprene have similar polar moieties as pendant groups and double bonds in the main polymer backbone. Buna N shows a decrease in compression set at t=200 hours which does not recover completely at t=1000 hours. On the other hand, Neoprene increases in compression set with time. For similar molecular structures, this opposite behavior for Neoprene may indicate that there may be molecular structure changes happening due to sCO2 interaction with this polymer that Buna N does not see. Buna N can interact with sCO2 with possible weak Vander Waal's interactions and this capture of sCO2 can increase the modulus "artificially" resulting in decreased compression set.

3.5 ATR-FTIR data for polymers in sCO2

FTIR was used to detect molecular changes in polymers after exposure to sCO2. The attenuated total reflectance method was used to make measurements on polymers before and after exposure to sCO2. For elastomers, there was significant change in molecular structure for the test conditions of exposure. For example with EPDM exposed to sCO2 at 150°C, all the peaks were present in the spectrum after exposure, but, they were reduced in peak height and intensity (Figure 22). This was also true for the EPDM specimens that had been through exposure to sCO2 at 100°C. For FF202 under the same conditions, all the peaks were present, but, it seemed that the -C-F peak at 1150-1000 cm-1 had shifted to longer wavelengths as well as changed in intensity. Also, the peak at 784 cm-1 had disappeared (bond scission?) after prolonged exposure to 150°C temperature (Figure 23). At 100°C, for the FF202, only the peak at 784 cm-1 had disappeared. All the others were still present. This indicates that the probability of occurrence of molecular changes in FF202 had increased with temperature.

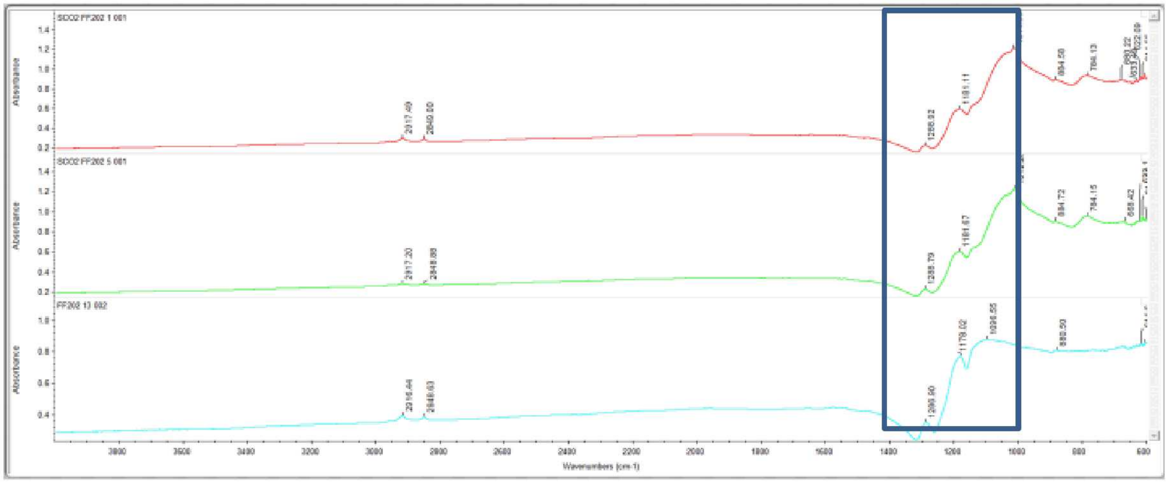
FTIR analyses of EPDM after SCO2 exposure for 0, 200 and 1000 hours at 150C



All the peaks are still present only seem a little decreased in peak height indicating some change with temperature such as bond scission

Figure 22. FTIR analyses of EPDM after SCO2 exposure at 150°C for 0, 200 and 1000 hours

FTIR analyses of FF202 after SCO2 exposure for 0, 200 and 1000 hours at 150C



All the peaks are still present: it seems that at 1000 hours, the C-F 1150-1000 cm^{-1} has shifted to the longer wavelengths as well as changed its intensity, peak at 784 cm^{-1} has disappeared (maybe some bond scission has occurred) dur to prolonged exposure to 150C temperature)

Figure 23. FTIR analyses of FF202 after SCO2 exposure at 150°C for 0, 200 and 1000 hours

For Nylon, there were no changes seen due to sCO2 exposure. All the peaks were unchanged and non-shifted (Figure 24). For PTFE, no significant changes were seen after exposure (Figure 25). For PEEK, the peak intensity at 2800-3000 cm-1 lowered in intensity and then recovered after 1000 hours (Figure 26). Peaks at 2800-3000 cm-1 represent the -C-H alkane stretching frequencies in these polymers. Their reduction/disappearance indicates a permanent change in the PEEK molecule.

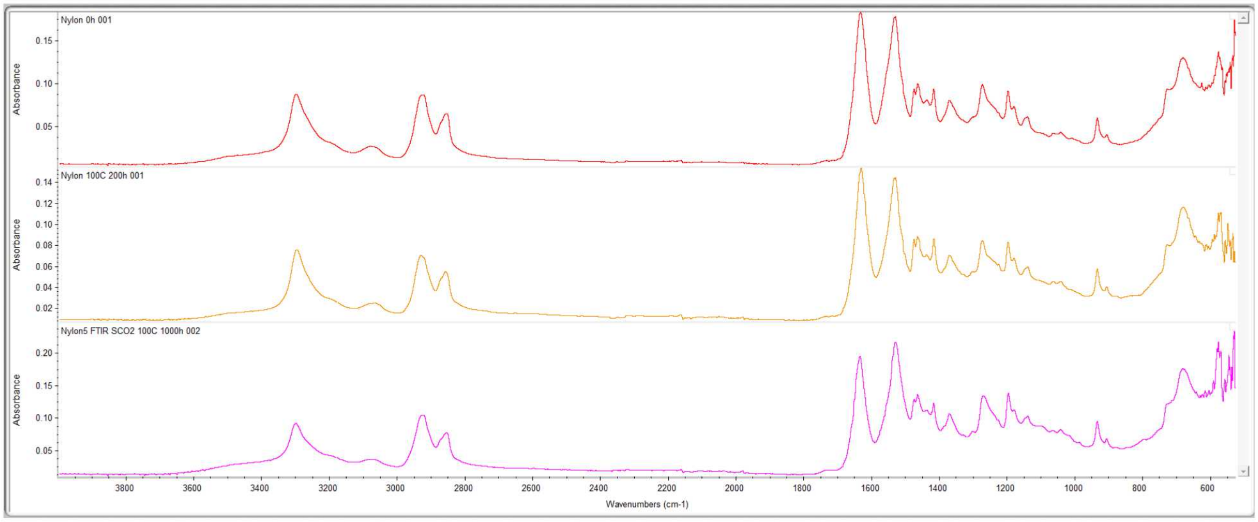


Figure 24. FTIR analyses of Nylon after SCO2 exposure at 100°C for 0, 200 and 1000 hours

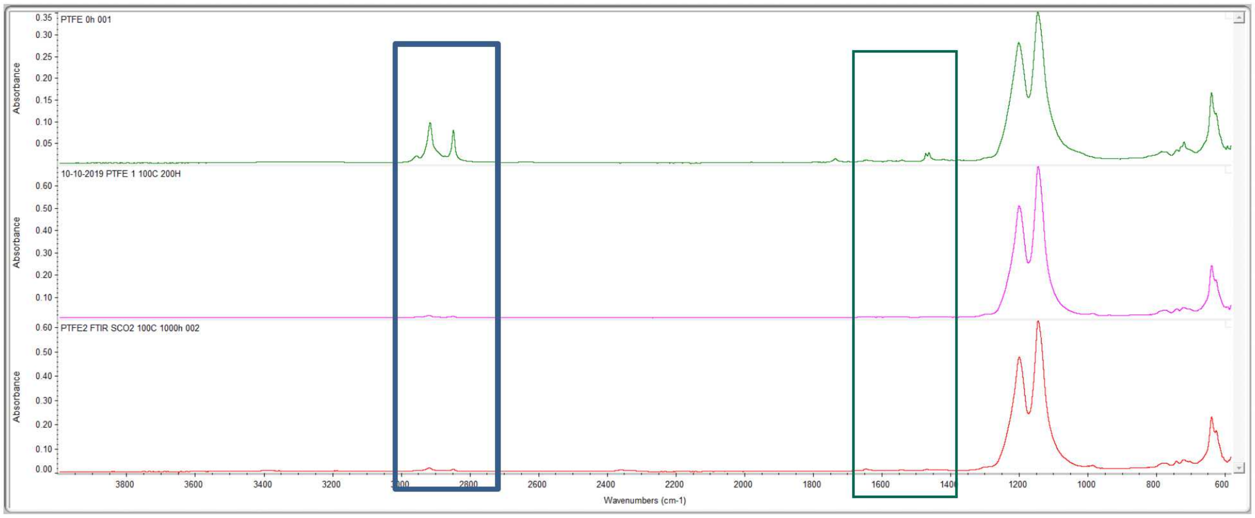


Figure 25. FTIR analyses of PTFE after SCO2 exposure at 100°C for 0, 200 and 1000 hours

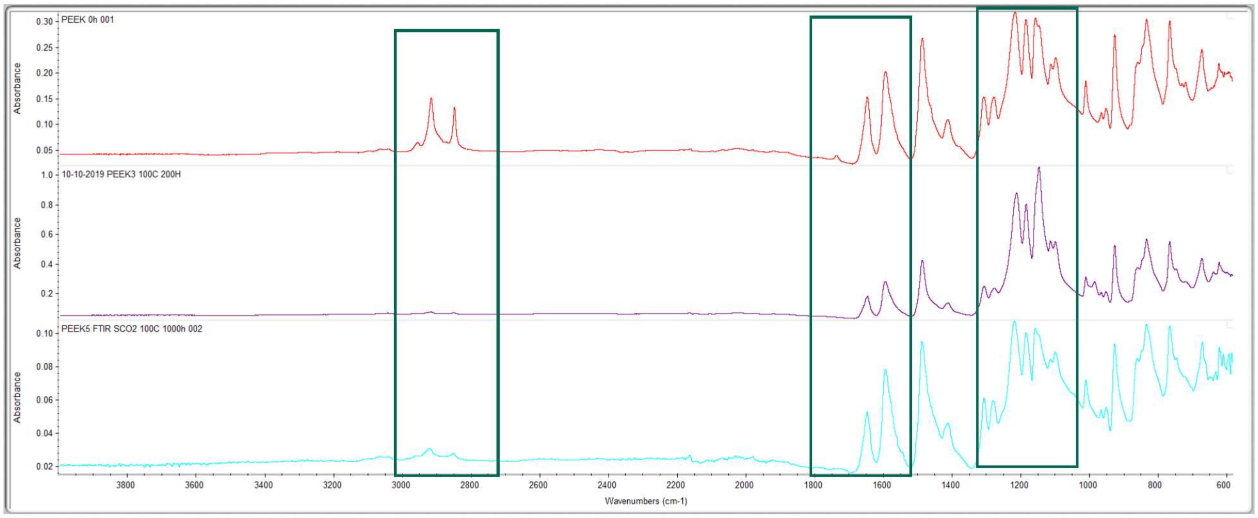


Figure 26. FTIR analyses of PEEK after SCO2 exposure at 100°C for 0, 200 and 1000 hours

Buna N and EPR did not show any changes in spectrum and remained the same before and after sCO2 exposure. However, Neoprene showed significant changes after exposure (Figure 27). Broad intense peaks appeared at 1400 cm-1 and 1600 cm-1 for t=200 hours and t=1000 hours. The two frequencies pertain to -O-H and -C=O groups respectively. Neoprene is chemically attacked by sCO2 and undergoes permanent chemical changes upon exposure.

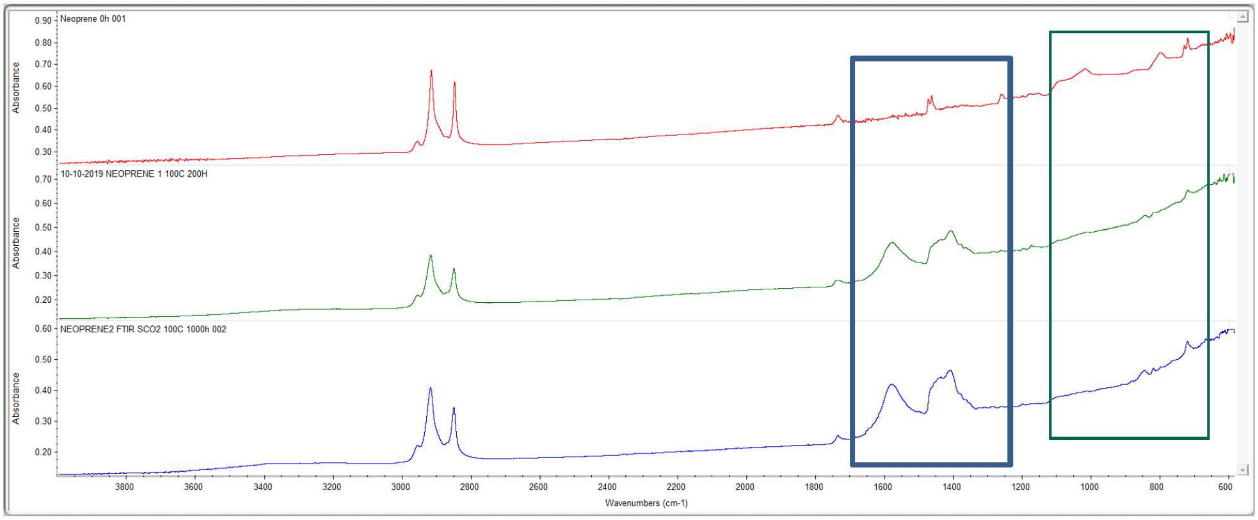


Figure 27. FTIR analyses of Neoprene after SCO2 exposure at 100°C for 0, 200 and 1000 hours

3.6 Optical microscopy imaging of polymers in sCO2

Optical microscopy was used to study surface changes and texturization effects on the polymers exposed to sCO2 at 150°C and 100°C. Surface attack was evident for some polymers at high magnifications. In some polymers, though the surface was not worn out, there was a ring flattening effect that was clearly seen. FF202 showed this flattening effect in the middle region of the O-ring at 100°C (Figure 28). FF202 also showed a roughening effect which could indicate sCO2 attack after prolonged times (Figure 29). EPDM (Figure 30), and PEEK (Figure 31) showed a smoothening effect with exposure to 1000 hours of sCO2 at 100°C. EPR (Figure 312) rubber had deep striations parallel to the axis of the O-ring which were starting to form cracks parallel to the axis with significant amount of polymer dust on the surface. Buna N (Figure 33) showed some striations perpendicular to the axis of the O-ring. Nylon O-rings did not show any damage due to sCO2 exposure (Figure 34). PTFE (Figure 35) also showed striations perpendicular to the O-ring axis. Viton (Figure 36) showed a large visible crack about 1000 microns long on the surface. Neoprene (Figure 37) showed the worst damage of all with severe erosion of material from the surface with formation of network of pores and wrinkling.

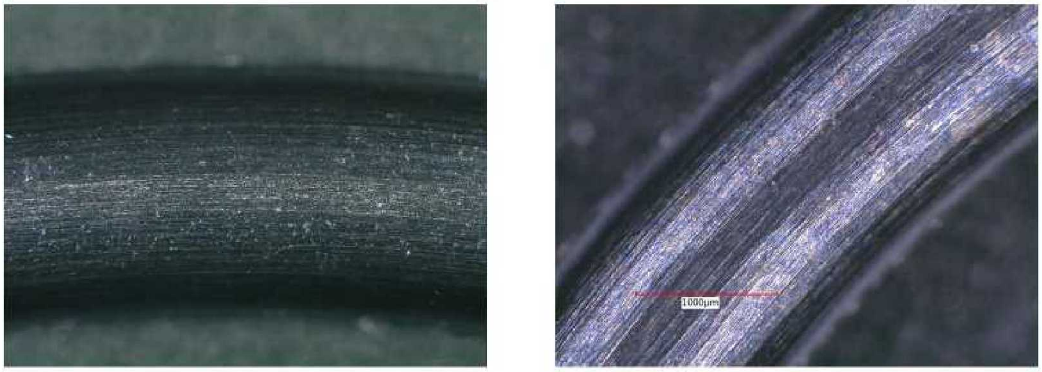
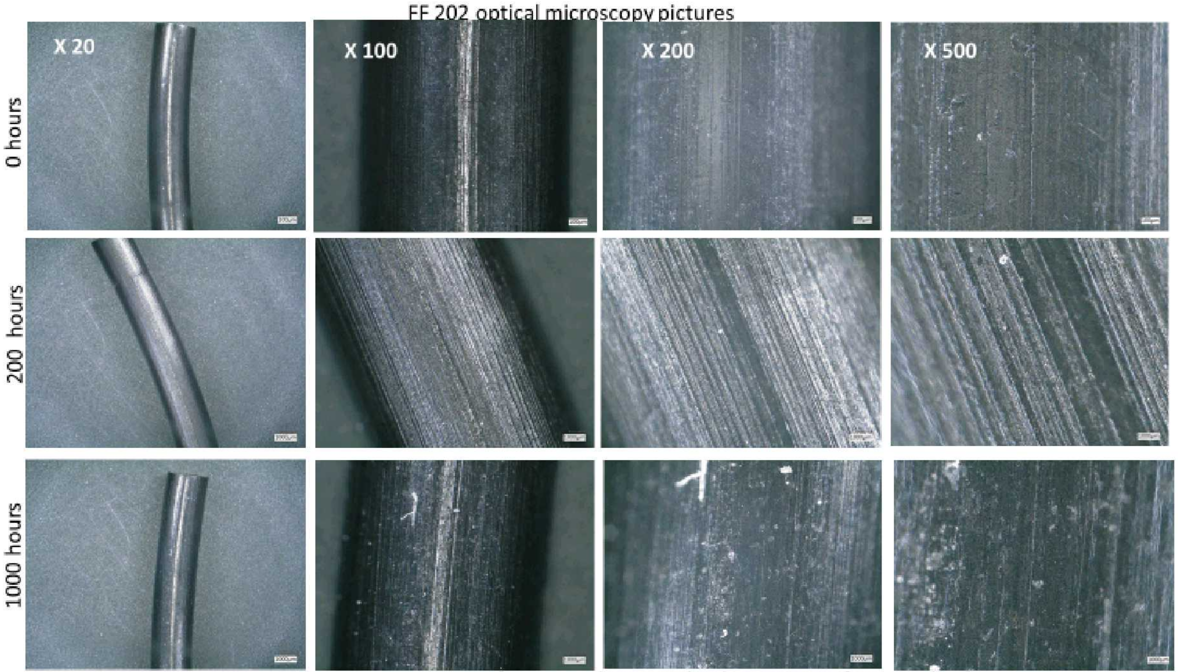


Figure 28. FF202 O-ring showing a flattening effect after sCO2 exposure at 100°C for 1000 hours

FF 202 optical microscopy pictures



Does exposure to SCO2 for a 1000 hours make the FF202 surface rougher?

Figure 29. FF202 before and after exposure to sCO2 for 0, 200 and 1000 hours

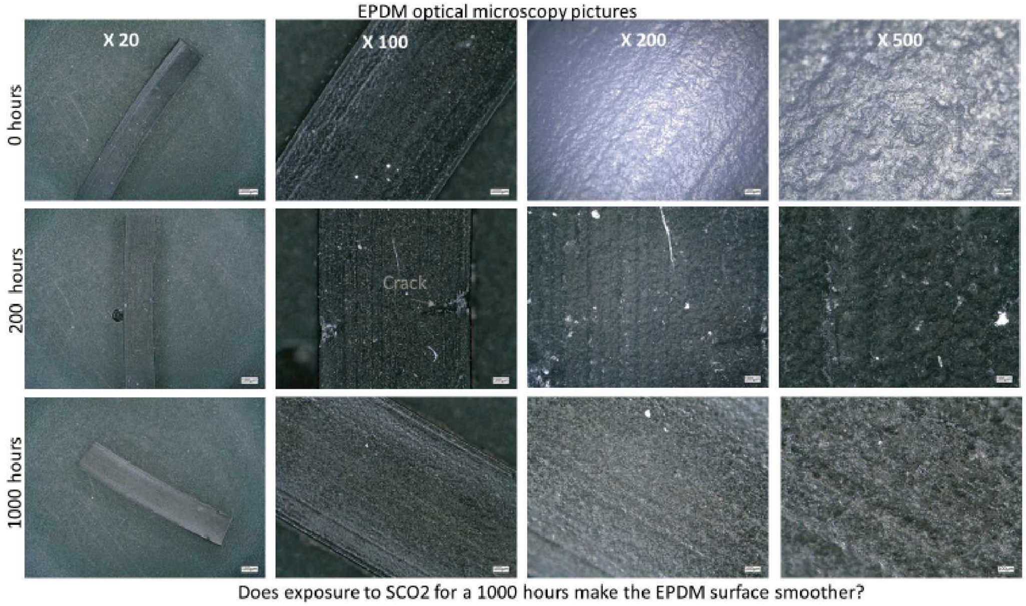


Figure 30. EPDM before and after exposure to sCO2 for 0, 200 and 1000 hours

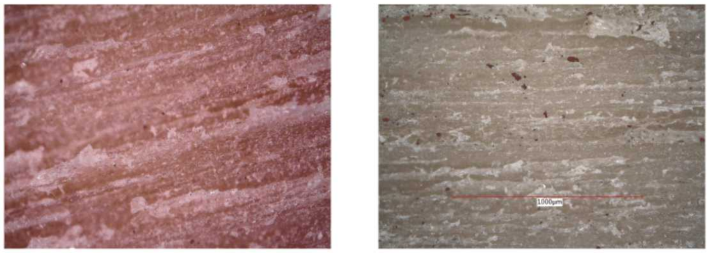


Figure 31. PEEK before and after exposure to sCO2 for 1000 hours

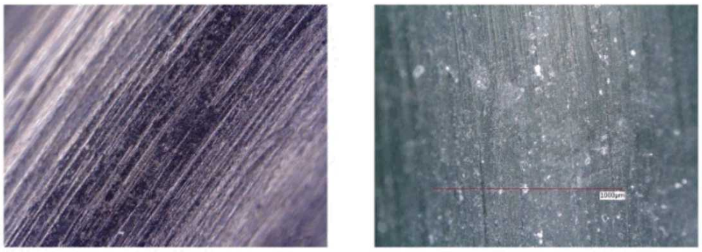


Figure 32. EPR before and after exposure to sCO2 for 1000 hours

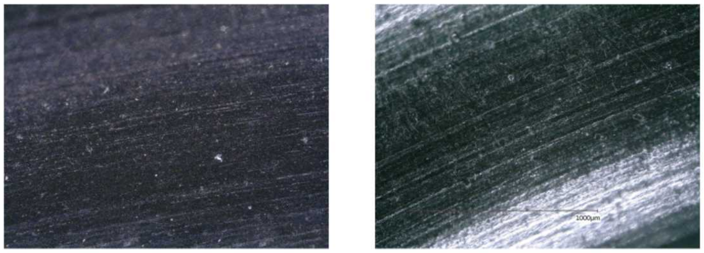


Figure 33. Buna N before and after exposure to sCO2 for 1000 hours

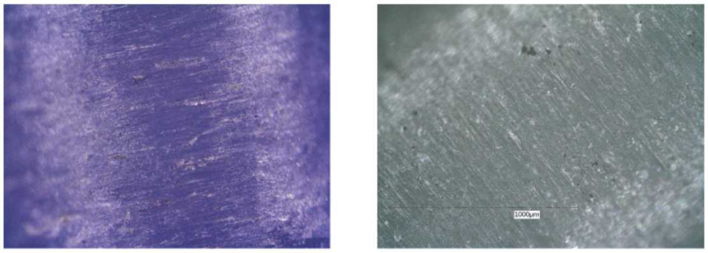


Figure 34. Nylon before and after exposure to sCO2 for 1000 hours

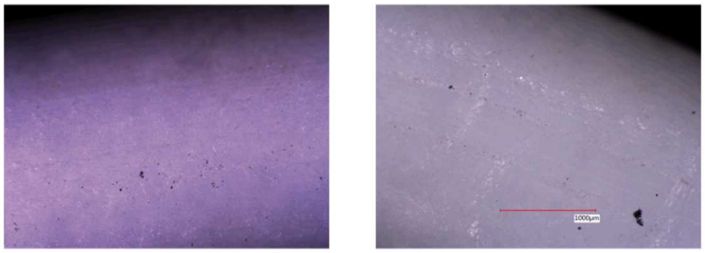


Figure 35. PTFE before and after exposure to sCO2 for 1000 hours

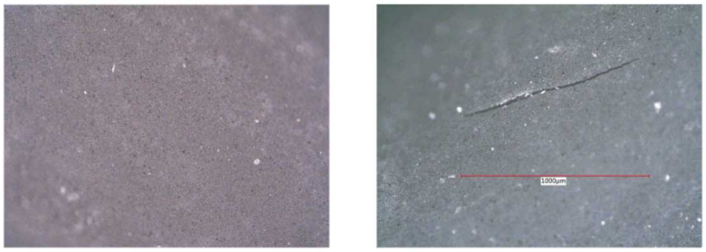


Figure 36. Viton before and after exposure to sCO2 for 1000 hours

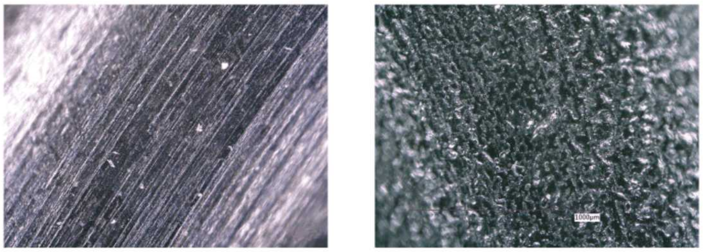


Figure 37. Neoprene before and after exposure to sCO2 for hours

3.7 Micro-CT data for polymers exposed to sCO2

Micro CT was useful in examining the polymers exposed to sCO2 for internal voids and cracks that were not visible from the outside. Only select polymers were examined using this technique because of the complexity of sample preparation and time needed to run this analysis. EPDM and FF202 that were exposed to 20 MPa of SCO2 at 150°C and 100 C were examined using this technique.

For EPDM at 100°C after 1000 hours, there was one large crack (about 720 microns long) near the surface of the O-ring with no evidence of any starting point for this crack. For EPDM at 150°C after 1000 hours, there were multiple cracks which were formed in random directions. These cracks seem to have started at 200 hours of expoure (Figure 38). For FF202 at 100°C/1000 hours, there was a long crack about 2000 microns long that seemed to have originated from an agglomerated filler particle in the matrix (Figure 39). For the same polymer at 150°C/1000 hours, many cracks there were paralle to the axis of the O-ring had formed. These were present at t=200 hours but increased in number with prolonged exposure. It is clear that for these polymers, longer exposure times and higher temperatures in sCO2 can give rise to damage in the form of short cracks (in EPDM) and long cracks parllel to the axis (in FF202).

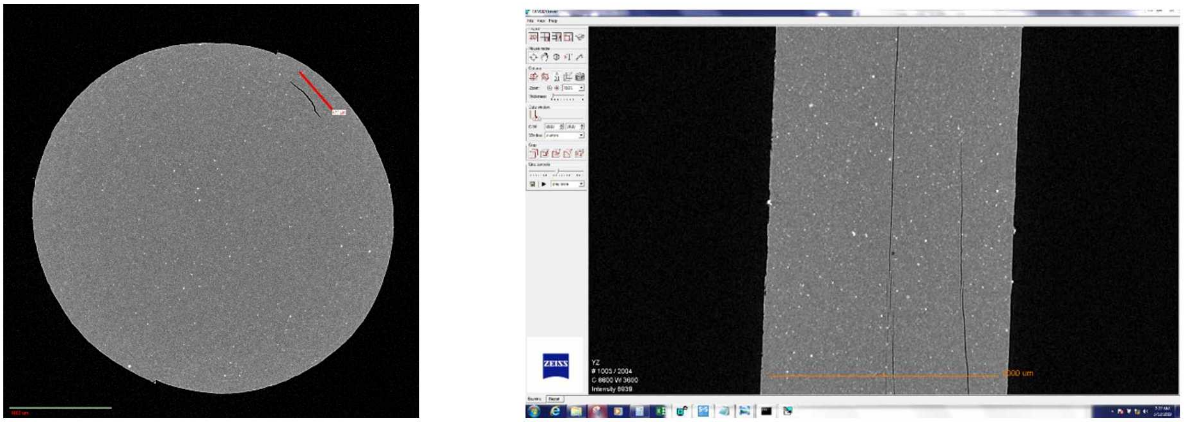


Figure 38. Images showing the 720 micron crack originating in sCO2-exposed near the surface of EPDM at 100°C/1000 hours (left) and multiple cracks after 150°C/1000 hours of exposure (right)

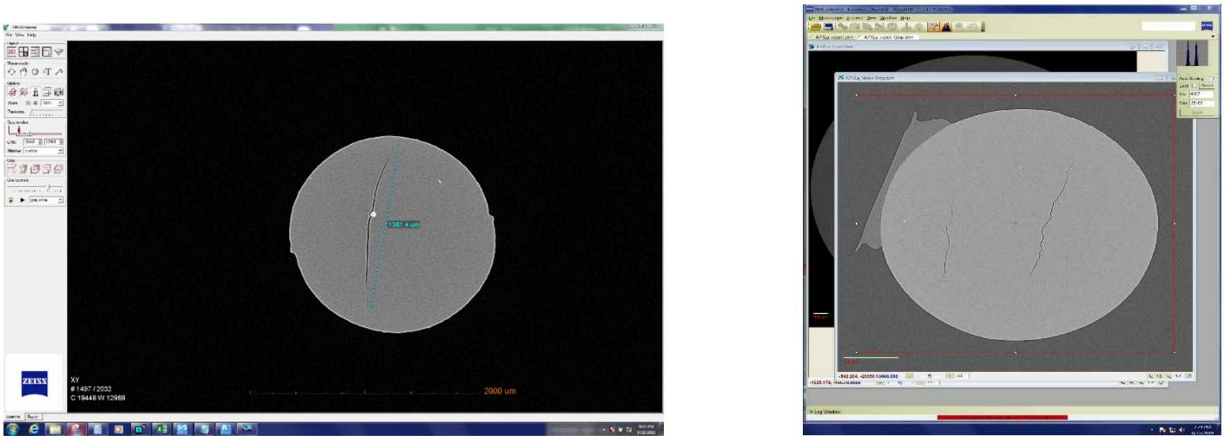


Figure 39. Images showing the 2000-micron crack originating around an agglomerate (left) in sCO2-exposed FF202 at 100°C/1000 hours and multiple cracks after 150°C/1000 hours of exposure (right)

4. CONCLUSIONS

Polymers such as FF202, EPDM, PEEK, Nylon, Neoprene, PTFE, Viton, EPR and Buna N commonly found in sCO2 energy conversion systems were exposed to 20 MPa of sCO2 pressure at 150°C and 100°C for 1000 hours. Samples were withdrawn at t=200 hours and at the end of the test and characterized for physical and chemical effects because of the exposure. Physical effects were seen in the form of changes in mechanical properties such storage modulus and in cracks and surface texturization changes in the polymers. Chemical changes were seen in the form of changes in glass transition temperatures, molecular changes in FTIR spectra and permanent deformation measured as compression set.

A couple of interesting observations are as follows. Based on polymer property changes observed, it is speculated that polymers with -C-F bonds seem to be capable of slowing down diffusion of sCO2 through the free volume and at the same time, seem to be enabling the formation of weak Vander Waal's forces between the fluorine atom and the sCO2. Polymers with -C=O and -C-Cl and -C-CN such as PEEK, Nylon (-C=O), Neoprene (-C-Cl) and Buna N (-C-CN) groups on the backbone or as pendant groups seem to be capable of the same interactions with sCO2. These Vander Wal's interactions when polymers are exposed to sCO2 seem to result in higher modulus for these polymers with or without change in glass transition temperatures. EPDM and EPR were not susceptible to changes due to sCO2 to a great extent because of their non-polar nature.

Overall thermoplastics showed the least molecular changes, the least swelling and negligible changes in modulus and glass transition with exposure to sCO2. Elastomers showed the most dramatic changes in properties after exposure. Of the elastomers, EPDM and FF202 worked well for 100°C exposures. At elevated temperatures (150°C), FF202 seemed to be superior in performance.

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