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Aging Behavior and Performance Projections for a Polysulfide Elastomer

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Aging Behavior and Performance Projections for a Polysulfide Elastomer

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Abstract

The accelerated aging behavior and aging state of a 30 year old field retrieved polysulfide elastomer was examined. The material is used as an environmental thread sealant for a stainless steel bolt in a steel threaded insert in an aluminum assembly. It is a two component curable polysulfide elastomer that is commercially available in a similar formulation as was applied 30 years ago. The primary goal of this study was to establish if aging over 30 years under moderate aging conditions (mostly ambient temperature and humidity) resulted in significant property changes, or if accelerated aging could identify developing aging pathways which would prevent the extended use of this material.

The aging behavior of this material was examined in three ways: A traditional accelerated thermo-oxidative aging study between 95 to 140 °C which focused on physical and chemical properties changes, an evaluation of the underlying oxidation rates between RT and 125 °C, and an assessment of the aging state of a small 30 year old sample. All three data sets were used to establish aging characteristics, their time evolution, and to extrapolate the observed behavior to predict performance limits at RT.

The accelerated aging study revealed a relatively high average activation energy of ~130 kJ/mol which gives overconfident performance predictions. Oxidation rates showed a decreasing behavior with aging time and a lower E_a of ~84 kJ/mol from time-temperature superposition, but also predicted sufficient additional performance at RT. Consistent with these projections for extended RT performance, only small changes were observed for the 30 year old material. Extrapolations using this partially aged material also predict ongoing use as a viable option. Unexpected RT degradation could only develop into a concern should the oxidation rate not trend lower over time as was observed at elevated temperature. Considering all data acquired in this limited aging study, there are no immediately apparent concerns with this material for ongoing use.

ACKNOWLEDGEMENTS

We thank Lisa Deibler for providing us with a small sample of field aged and new commercial material.

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NOMENCLATURE

ATR	Attenuated Total Reflectance, a sampling technique for infrared spectroscopy
E _a	Activation Energy, usually reported in kJ/mol
IR	Infra Red spectroscopy
RT	Room Temperature, often used as ambient aging condition
SNL	Sandia National Laboratories
T _g	Glass Transition temperature

1 INTRODUCTION

This report documents a summary of the work we conducted from November 2013 through April 2015 in Org. 1853 Organic Materials Science at SNL. It relates to the characterization of a commercially available two component ‘Flamemaster CS3204’ polysulfide elastomer curable with MnO_2 as a catalyst. It is used as a thread sealant for a steel bolt which is screwed into a steel threaded insert located in an aluminum assembly. Curing is most likely accomplished via free radical oxidation of terminal thiol (-SH) groups. Polysulfides usually have a T_g in the range of -20 to -60°C , therefore under the normal use conditions this material is a rubbery elastomer. The material has no load bearing requirements; it is simply used as gap filler for voids between steel and aluminum offering some protection against local corrosion. The material has been in use for approximately 30 years, but little is known about its long-term degradation behavior. We were asked to conduct a screening study that would provide feedback on current state and expected aging behavior for re-qualification purposes.

2 GOALS OF THIS STUDY

- Establish primary pathways and sensitivity of this material to degradation.
- Conduct overview thermally accelerated aging study.
- Summarize all aging data and determine activation energies for property extrapolations.
- Identify reasonable changes in the material properties with accelerated aging exposure to determine time data for transition from moderately aged material to major aging state.
- Prepare time temperature superposition plots for all property changes under accelerated aging conditions and establish accelerative shift factors.
- Measure a limited data set for oxidation rate measurements and obtain shift factors from superposition of oxidation levels with time and temperature.
- Prepare Arrhenius plot of all shift factors and establish correlations between oxidation level and physical property changes.
- Prepare overview Arrhenius plot for projection of performance at lower temperatures incorporating all available time data for reasonable property and oxidation levels which would be regarded as acceptable “aging levels”.
- Rate aging state of the field returned material based on accelerated aging and characterization testing.
- Provide extended performance predictions for ongoing use of existing sealant based on accelerated aging extrapolations, oxidation level predictions using the most reasonable rate behaviors, and assessment of limited property changes from field returned ‘30 year old’ material.

2.1 Thermal aging study of polysulfide elastomer

A limited thermal aging study was performed at 95, 110, 125 and 140°C. It was anticipated that these aging temperatures would yield property changes within a reasonable time-frame. Lower aging temperatures would be preferred, but time and budget constraints did not allow for an extended aging study. Further, the low temperature behavior was intended to be additionally probed by oxidation rate measurements. For the accelerated thermal aging study samples were taken at variable time intervals based on the aging behavior observed, with the highest temperature providing early guidance. Property changes were examined as:

- Tensile testing of 5 mm wide and 1 mm thick test strips to obtain strain and load at failure, as well as initial elastic modulus. Modulus was determined between a load of 50 and 100 ksi. Tensile testing is sensitive to embrittlement and elastomer network changes and is commonly used as a convenient indicator for property changes during aging of elastomers. The material has no load bearing requirements; therefore, this aging study did not require any specialized mechanical characterization. However, embrittlement or partial disintegration may facilitate localized corrosion.
- Elastic elongation (strain) under a limited static load of 1 lbs.
- Polymer network analysis to examine crosslinking or scission dominated degradation processes of samples solvent extracted under refluxing toluene. Gel content (total crosslinked material) is obtained as the ratio of toluene insoluble to initial weight of the material, and solvent uptake factor (network strength where a higher number means more swelling or less tightly bound gel) is obtained as the total weight of solvent and gel divided by the weight of dried gel.
- Assessment of oxidation levels as carbonyl formation at $\sim 1730\text{ cm}^{-1}$ (widely used signature of degradation chemistry) using IR spectroscopy.

2.2 Oxidation rates of polysulfide elastomer

A limited oxidation rate study within the given time constraints of this project was performed at RT to 125°C. Samples were cumulatively exposed to air in sealed ampoules and the underlying oxidation rates quantified, based on the oxygen loss in a sealed volume under these conditions. This yielded the oxidation rate in mols/g-s, an intrinsic material property, as a measure of the thermo-oxidative degradation tendency of this material. The technique for measuring oxidation rates has been discussed in the past and is often used to provide a perspective on the reactivity of polymers at low temperatures [1,2]. This approach often provides additional aging information that traditional aging studies cannot obtain [3-5].

- Oxidation rates were measured with cumulative exposure time at RT, 50, 95 and 125°C.
- Time temperature shift factors were determined via a data superposition of oxidation levels with time and temperature.

- Oxidation rates were found to decrease over time. This is not the most common behavior, but has been observed for some materials in the past. For example, decreasing rates have been observed for Hypalon, butyl elastomers, and some epoxies. Oxidation is not always constant with time; sometime rates are quite steady and sometimes rates increase or decrease with changing oxidation levels.

2.3 Limited screening of hydrolytic degradation tendency of polysulfide elastomer

A limited exposure to water and elevated temperature was conducted only to assess whether hydrolytic degradation can affect this material at all and if scission or crosslinking processes could be detected. This was a limited screening attempt. An extended study was not possible due to budget constraints and the nature of more complicated experiments, which would be required to rate material degradation in comparison with thermo-oxidative aging. SNL has invested few efforts for expertise in hydrolytic aging of polymers in the past and such experiments are not straight forward. Should such phenomena be of interest, then more substantial research effort should be facilitated.

- The effects of water exposure were monitored for a few selective samples immersed at 95°C for 35, 70 and 105 days.
- A clear trend of material softening and expansion was observed. This visual evidence of polymer network scissioning was corroborated by a significant drop in gel content with aging time. A sample immersed in water at 80°C for 362 days had significant hydrolytic damage resulting in a gum-like material with significant loss of elasticity. This sample disintegrated into several smaller pieces during toluene reflux which indicates significant loss of network integrity.
- Hydrolytic degradation was found to be a possible accelerated aging process based on this limited high temperature water-immersion screening, but is not deemed important for the field aging of this material. Characterization testing (gel content, uptake factor, and elastic modulus) of the field retrieved material suggests thermo-oxidatively driven crosslinking was the dominant aging pathway for this material over its 30 year history.

3 KEY CONCLUSIONS

- Accelerated thermal aging provided time-temperature superposition shift factors for a number of properties. Thermal aging between 95 and 140°C yielded relative high activation energies (E_a) in the range of 108 to 149 kJ/mol. These were obtained for carbonyl formation and mechanical properties such as tensile modulus, elastic load modulus, maximum tensile strain, gel content and uptake factor, all together yielding an average E_a of 127 kJ/mol.
- The relevant times required to induce significant changes in these properties described as a ‘threshold aging state’ which separates moderate acceptable aging states from more significant aging levels were also obtained and extrapolated to RT.
- In comparison, oxidation rate measurements yielded a lower activation energy of 84 kJ/mol and strong evidence that oxidation rates tend to decrease over time.
- This means that under accelerated conditions there is limited correlation between oxidation level and physical property changes. A discrepancy between oxidation chemistry levels and physical changes is not always the case in polymer aging, but certainly is clearly established for the material investigated here. Nevertheless, it is clear that the above property changes are related to oxidation and 2% oxidation extent is indicative of moderate to significant aging related material changes.
- As a consequence of the differences in the activation energies, different performance projections result from oxidation rates and physical properties such as modulus, tensile strain at failure or elastomeric network properties. A performance projection was obtained as the average extrapolated time of specific material states in physical properties which are regarded as acceptable changes or moderate aging levels.
- Extrapolation of elevated temperature physical property changes yields significant material stability at lower temperature, primarily due to the high activation energies involved. It is clear that a performance projection of thousands of years is overly conservative and does not take into account any mechanistic changes that may develop at lower temperatures. Mechanistic changes are often picked up by oxidation rates which have yielded curved Arrhenius plots in the past.[3]
- A more reasonable estimation is given by time extrapolations to reach 2% oxidation level at lower temperatures. However, since the oxidation rates trend lower over time with increasing oxidation level, significant material stability or sufficient performance is still projected (380 years at RT).
- Only under a worst case scenario assuming a steady RT oxidation rate ($1e-12$ mols/g-s) does the projected material performance fall into a potentially performance limiting regime of ~ 20 years. However, the material has already performed for 30 years with little loss in properties. Further, there is measured evidence that the oxidation rate declines at RT. Therefore, a constant rate at RT is unlikely and only discussed here to

show a worst case boundary condition. Only a slightly lower average rate will push this material towards ongoing satisfactory performance for requalification needs.

- An assessment and rating of the field returned material (30 years of use) revealed that only limited aging had occurred in this material. This was apparent in limited changes for modulus and gel content or uptake factor. The observed changes are within the beginning of those observed under accelerated conditions and represent only a fraction of what the material can accommodate. Interestingly, the material crosslinks (higher gel and lower uptake factor) under thermo-oxidative, but scissions under hydrolytic conditions. In a sense, thermal and moisture driven processes have a tendency to counteract each other. However, the observed changes in the field returned material are fully consistent with a thermo-oxidatively driven crosslinking dominant aging process and not hydrolysis. It is not possible to directly measure the existing oxidation level, but the material had low carbonyl, and based on this and its uptake factor we estimate the oxidation level to be below 1%. The predicted oxidation rate behavior and oxidation level evolution at RT gives ~0.6 % oxidation which should have occurred over 30 years.

4 RECOMMENDATIONS

- Based on these observations we conclude that there is evidence for some mechanistic differences in the evolution of physical property changes and chemically driven oxidation processes under accelerated aging conditions for this material. Physical property changes project sufficient additional performance margins with in fact unrealistically slow aging at RT. Since oxidation rates showed a lower activation energy they yield more realistic extrapolations, but also suggest sufficient long-term material performance. This is given by key trends showing that the oxidation rates decrease over time, i.e. are degradation level dependent as documented by the rate behavior at elevated temperature. Only a constant RT oxidation rate would push the aging process into a marginal regime for requalification purposes. This is unlikely to happen, but sufficient RT data as part of this limited aging study could not be obtained to rule out this possibility.
- Based on projections of accelerated aging data, oxidation rate measurements and the measured properties of the field returned material (elastomer network state and modulus), we conclude that only limited aging has occurred during 30 years of field use and that a sufficient reserve performance margin exists for at least another 40 years.
- While the expected material lifespan exceeds current requalification demands, predictions of extended operational life must be treated with some cognizance that the uncertainty bounds are not quantified, and that an extensive aging study involving a rigorous combination of thermal and hydrolytic aging processes was not conducted. However, all the evidence obtained in this study (accelerated aging, oxidation rates, and field returned material) and careful interpretation of extrapolations supports requalification.

5 VISUAL SUPPORTING INFORMATION TO DOCUMENT EXPTL. OBSERVATIONS

Polysulfide Lug Sealant Aging Study

Material: Polysulfide elastomer used as elastomeric sealant, two component Flamemaster CS 3204

Concern: Elastomer aging results in brittle material and perhaps a compromised seal performance

Approach: Conduct aging study using newly obtained material
Rate aging state of existing retrieved material

Experimental work:

- Prepare tensile specimens for accelerated aging study
- Conduct oxidation rate measurements for extrapolation to lower T
- Probe elastomer network (elasticity properties) for samples of aging study and compare with retrieved material
- Rate field retrieved material with IR for aging state after 30 years



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Flamemaster cure conditions

Material: Flamemaster CS 3204, Class B, Type 2, Aircraft Integral Fuel Tank Sealant

CS 3204 is a two-part polysulfide base compound which cures at room temperature to a flexible, resilient rubber with excellent adhesion to aluminum, magnesium, titanium, steel, and numerous other materials. CS 3204 is designed to withstand the attack of sulfur compounds that are present in jet fuels. When mixed, CS 3204 Class A is a self leveling liquid. CS 3204 Class B is a thixotropic paste that will not flow or sag on vertical or overhead surfaces.

Specified application and cure schedules are based on the standard conditions of 77°F and 50% relative humidity.

A/B = 10:1

Part A is an aliphatic polysulfide polymer < 60% (CAS 68611-50-7) + toluene < 4%

Part B is manganese dioxide < 65%, crosslinking catalyst for -SH

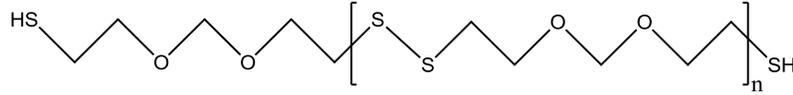
WORK LIFE	APPLICATION TIME	TACK FREE TIME	CURING RATE TO 35 SHORE A
**1/4	1/4 HOUR	6 HOURS	16 HOURS
1/2	1/2 HOUR	8 HOURS	30 HOURS
1	1 HOUR	15 HOURS	40 HOURS
2	2 HOURS	24 HOURS	72 HOURS
4	4 HOURS	36 HOURS	90 HOURS

Material is a two component crosslinkable aliphatic polysulfide elastomer

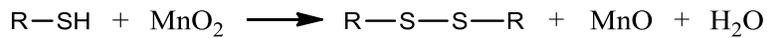
2

Material background information

- The Flamemaster polysulfide precursor material is a thiol terminated polyether oligomer given by the general structure:



- Polymerization/crosslinking is accomplished by oxidizing the thiol end groups with manganese dioxide (MnO_2) to form disulfide bonds.

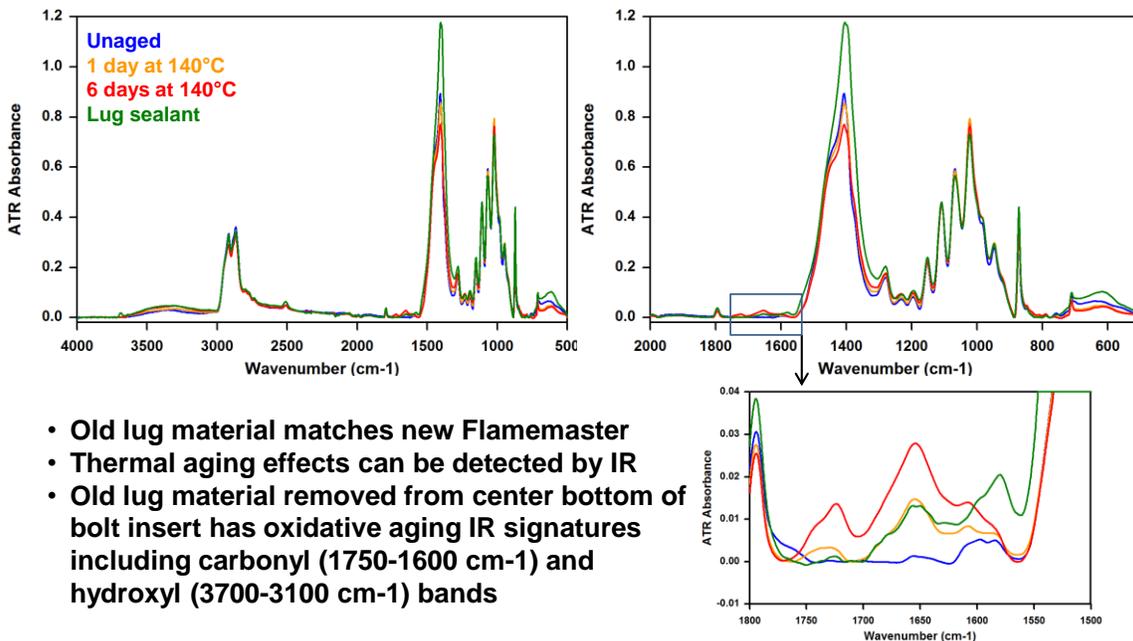


- Degradation has been discussed as S-S cleavage and rearrangement and traditional free radical CH_2 oxidation leading to crosslinking. It is less clear how hydrolysis should proceed, however some ether hydrolysis has been suggested.

3

Material identification via IR spectroscopy

- IR spectroscopy can be used to verify that field retrieved lug sealant and Flamemaster CS-3204-B-2 are the same material

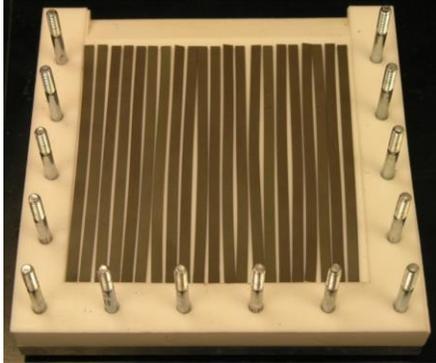


- Old lug material matches new Flamemaster
- Thermal aging effects can be detected by IR
- Old lug material removed from center bottom of bolt insert has oxidative aging IR signatures including carbonyl (1750-1600 cm^{-1}) and hydroxyl (3700-3100 cm^{-1}) bands

IR confirms that lug sealant and Flamemaster are the same polysulfide material 4

Cured material for limited aging study

- Seventy 147x5x1 mm tensile strips were prepared for limited thermo-oxidative aging at 140, 125, 110, & 95°C (~15 samples/T) and extended aging at 80°C (3 samples)
- Nine samples were set aside to screen for hydrolytic aging under water at 95°C



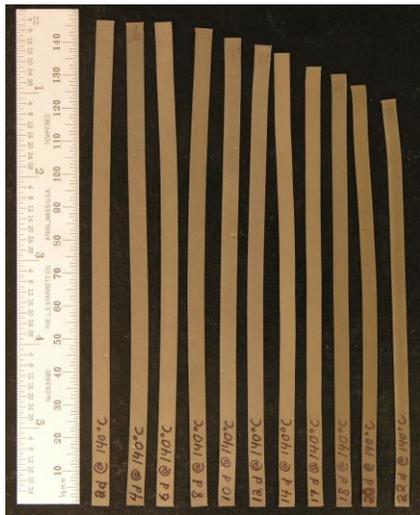
	LIMITED AGING STUDY
140°C	Pull every 2 days (22 days)
125°C	Pull every 4 days (64 days)
110°C	Pull every 10 days (150 days)
95°C	Pull every 25 days (400 days)
80°C	Continuous extended aging

- Thermal aging of polysulfide will be followed by:
- Mechanical property changes as tensile elongation and elastic elongation under load
- Polymer network changes as solvent uptake and gel content
- IR to probe chemical changes such as carbonyl growth (oxidation)
- Aging acceleration factors and threshold levels for property changes will be established

Seventy samples were prepared for a limited aging study

5

Accelerated aging and elastomer changes

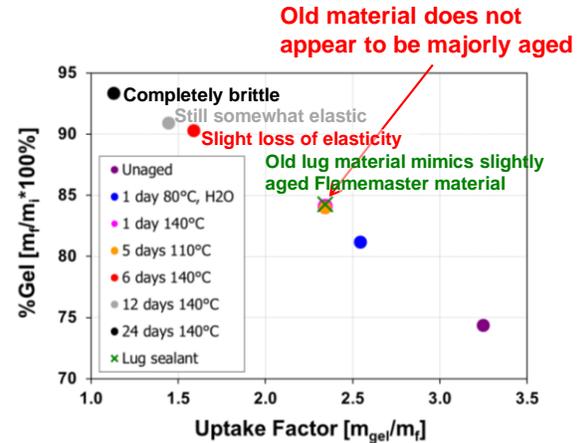
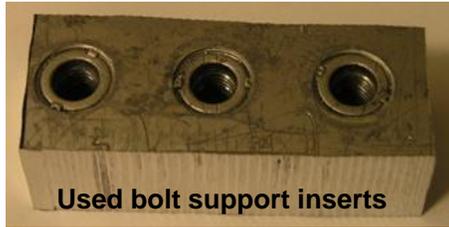


- Example of aged specimens ready for tensile testing
 - Severely accelerated aging at 140°C shows crosslinking and shrinkage
 - Testing was conducted at 95, 110, 125, 140°C
 - Screening if water may act differently
 - Hydrolytic aging of tensile specimens immersed in water at 95°C
 - Hot moisture appears to induce scissioning, expansion and softening
- Crosslinking versus scission aging processes
 - Thermal aging is dominated by crosslinking and hardening

6

Preliminary elastomer network analysis

- Chemical changes of the polymer network were probed on small samples immersed for ~18 hrs under refluxing toluene. The hot solvent extracts soluble polymer allowing the remaining gel content and swelling (uptake factor) of the gel to be determined.

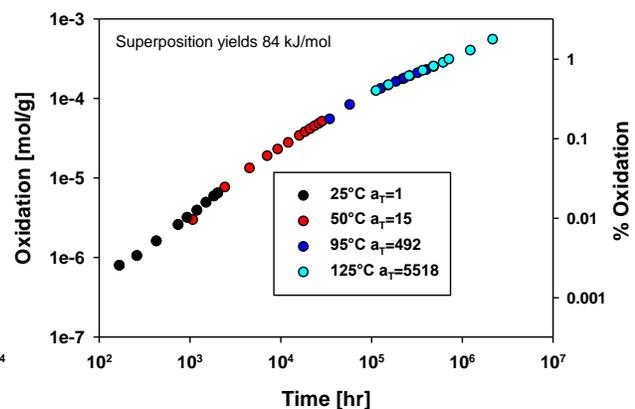
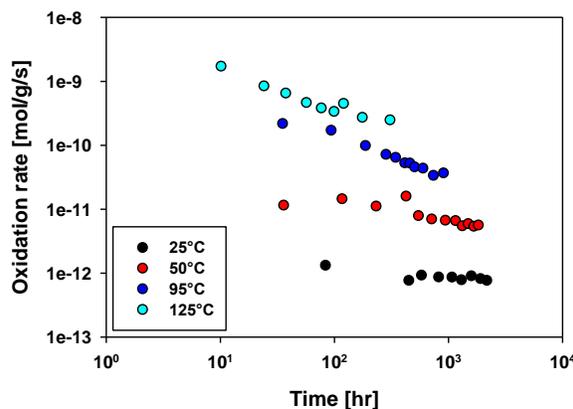


- Solvent extraction can be used to probe crosslink state of lug sealant
- Preliminary comparison suggests field retrieved material aging state is roughly equivalent to 5 days at 110°C or 1 day at 140°C

7

Oxidation rate measurements

- Oxidation rates allow for degradation chemistry to be quantified.
- Rates and oxidation levels can be correlated with other property changes.
- Rates can also be used to predict oxidation sensitivity and material oxidation behavior at lower temperatures.

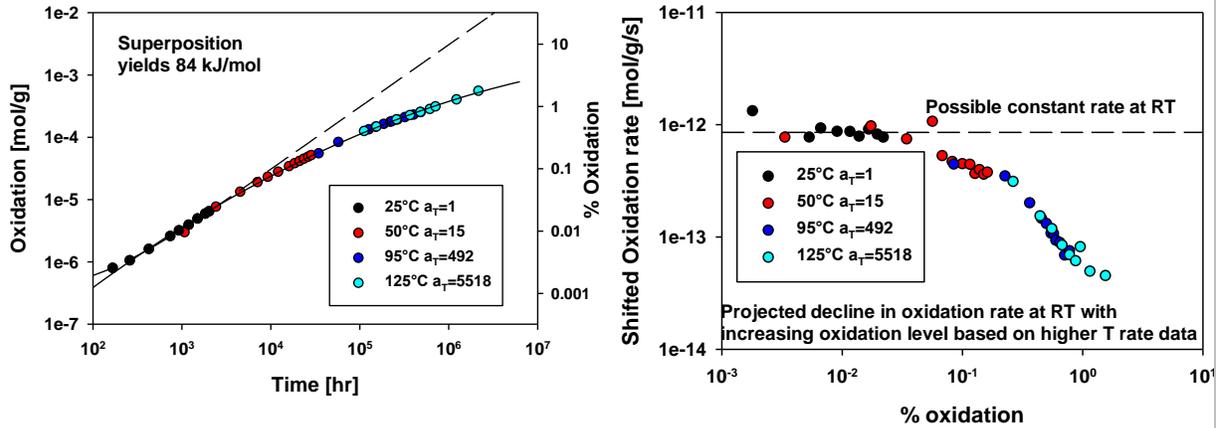


- The polysulfide elastomer shows a decreasing oxidation rate, i.e. the rate trends lower with increasing oxidation level
- This makes predictions more difficult; is the decrease independent of T?
- Measured 2% oxidation after 500h/125°C, 0.8% oxidation after 1000h/95°C

8

Oxidation rate measurements

- Oxidation rates change with aging time. This makes predictions challenging.
- Primary superposition assumes rates to decrease at all temperatures.
- Rates may also level off which will result in a faster oxidation level accumulation.
- However, evidence for rate decline was experimentally observed at 125, 95, 50°C

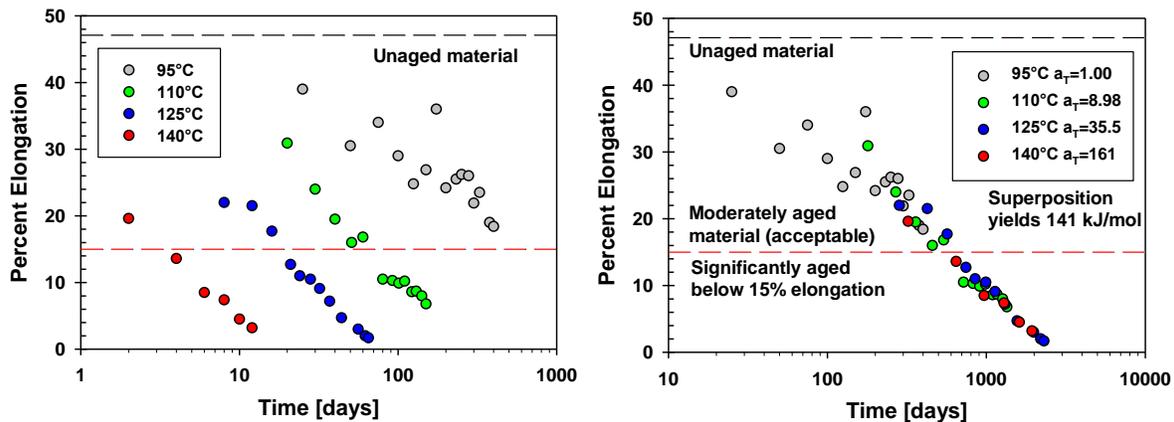


- Two different approaches can be applied to estimate oxidation levels during accelerated aging and extrapolate for specific %-oxidation at lower T
- Constant rates imply faster oxidation, whereas declining rates will suggest less oxidation with time and increased performance margins

9

Elastic elongation under load

- Elongation (EL) was measured for 10cm of the elastomer strips.
- EL was recorded 30 seconds after a 454.6 gram weight was applied.
- %Elong = (EL - 10 cm)/(10 cm)*100.

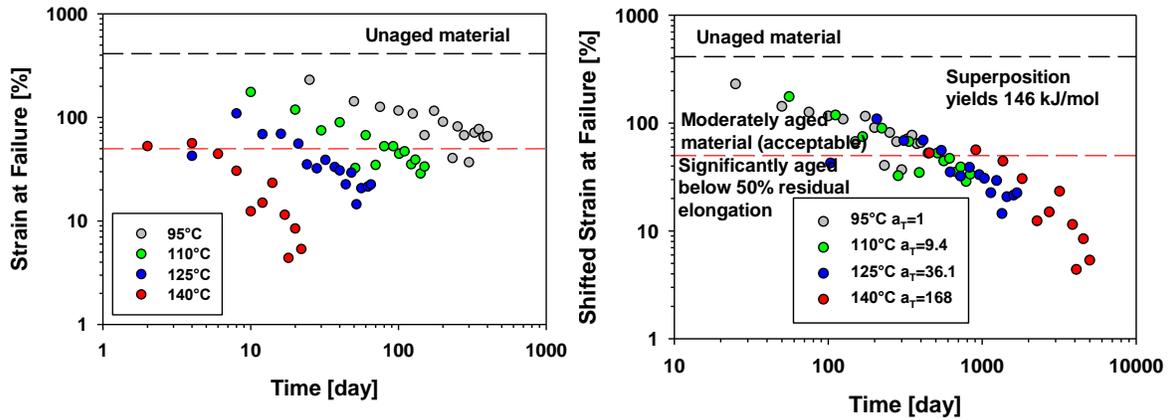


- Elastic elongation drops with aging, indicative of hardening/crosslinking
- Time to 15% elongation is used as an indicator for significant aging

10

Tensile testing – max. elongation

- Tensile testing was conducted on ¼” wide tensile strips with 2” separation between the crossheads at 1” per minute.
- Mechanical properties obtained: Max. strain and stress at failure, initial modulus
- Material is a weak elastomer which stretches easily under load.

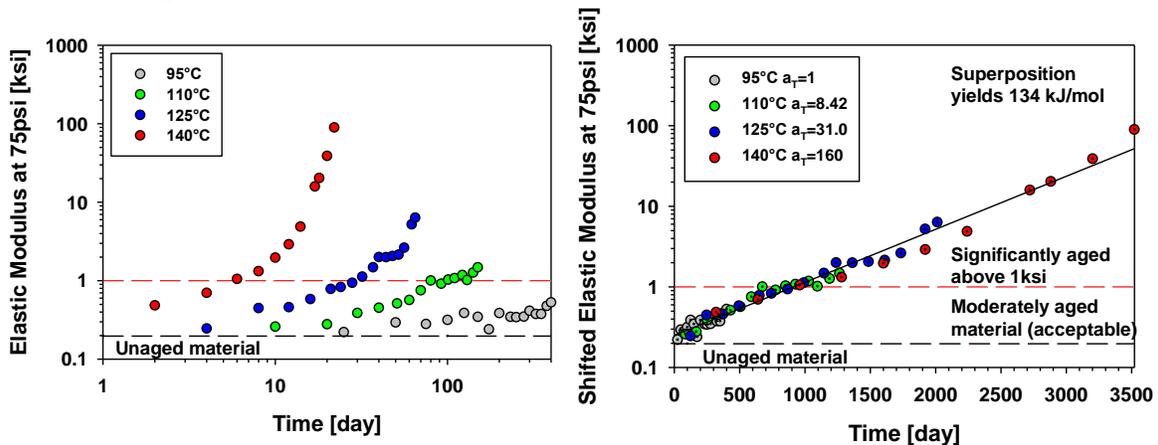


- Max. elongation (strain at failure) drops with aging indicative of hardening/crosslinking or a more brittle material
- Time to 50% absolute remaining elongation indicates significant aging

11

Tensile testing – initial elastic modulus

- Tensile testing was conducted on ¼” wide tensile strips with 2” separation between the crossheads at 1” per minute.
- Initial tensile modulus was determined between 50 and 100 psi.
- Unaged material ~ 0.2ksi (1.4 MPa), 1.0 MPa from modulus profiler

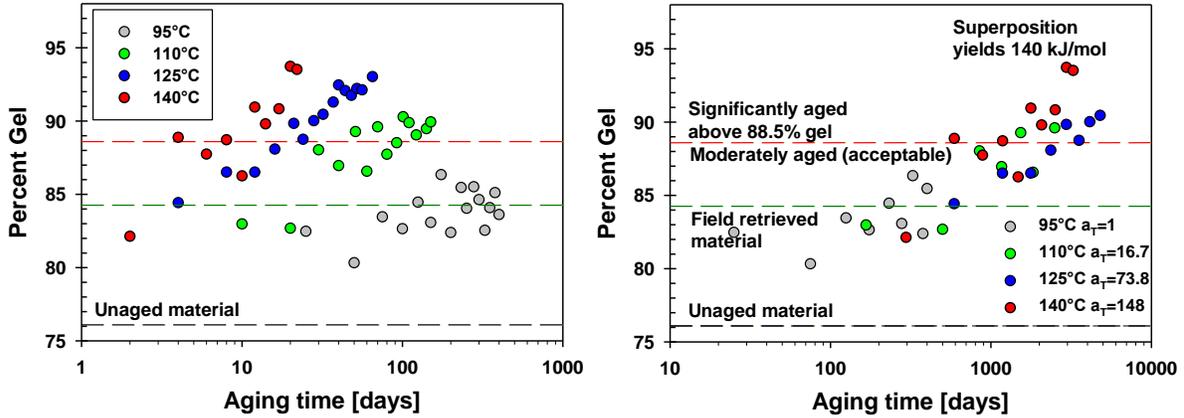


- Elastic modulus increases with aging, indicative of hardening/crosslinking or a more brittle material
- Increase to a modulus of 1 ksi (6.9 Mpa) indicates significant aging

12

Elastomer network analysis – gel content

- Chemical changes of the polymer network were probed on small samples immersed for ~18 hrs under refluxing toluene. The hot solvent extracts soluble polymer allowing the remaining gel content and swelling (uptake factor) of the gel to be determined.

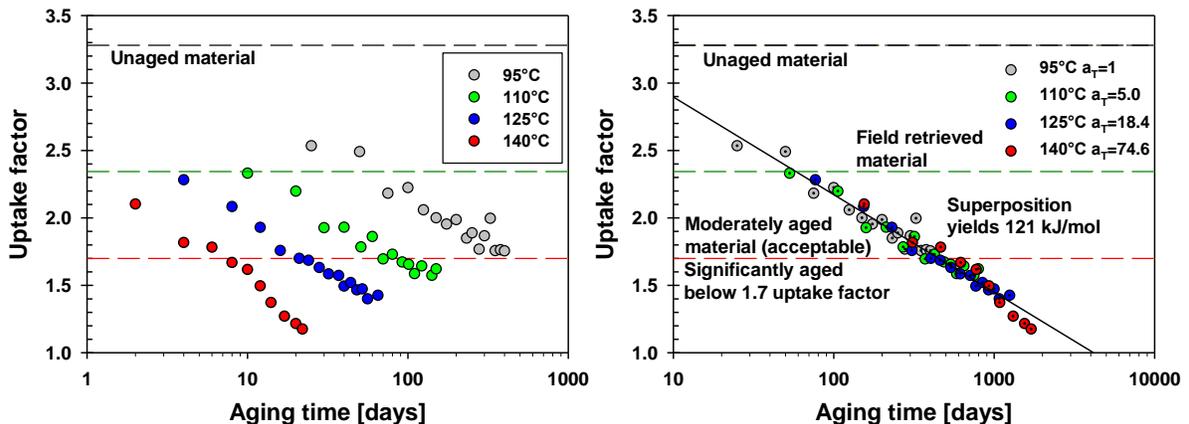


- Gel content increases and uptake factor (network strength) decreases with aging exposure
- Thermo-oxidative aging of this material is confirmed as crosslinking
- Increase to 88% gel content indicates significant aging

13

Elastomer network analysis – uptake factor

- Chemical changes of the polymer network were probed on small samples immersed for ~18 hrs under refluxing toluene. The hot solvent extracts soluble polymer allowing the remaining gel content and swelling (uptake factor) of the gel to be determined.

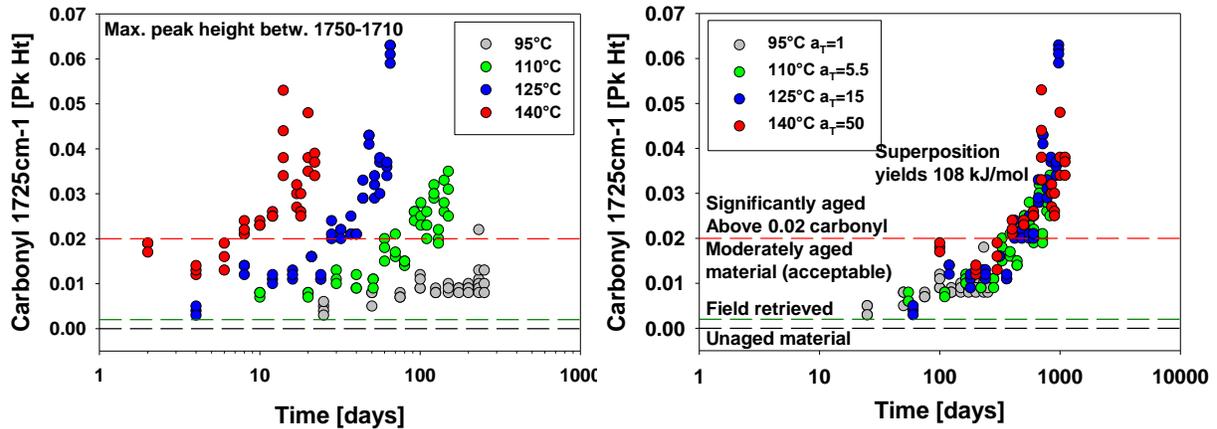


- Uptake factor (network strength) decreases with aging exposure
- Thermo-oxidative aging of this material is confirmed as crosslinking
- Decrease to 1.7% uptake factor indicates significant aging

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IR analysis – carbonyl formation

- Chemical changes of the polymer which probe oxidation extent were measured as carbonyl formation with IR spectroscopy.
- Carbonyl peak height was determined with contact ATR measurements in triplicate.
- Spectra were baseline corrected and normalized to 1404 cm⁻¹

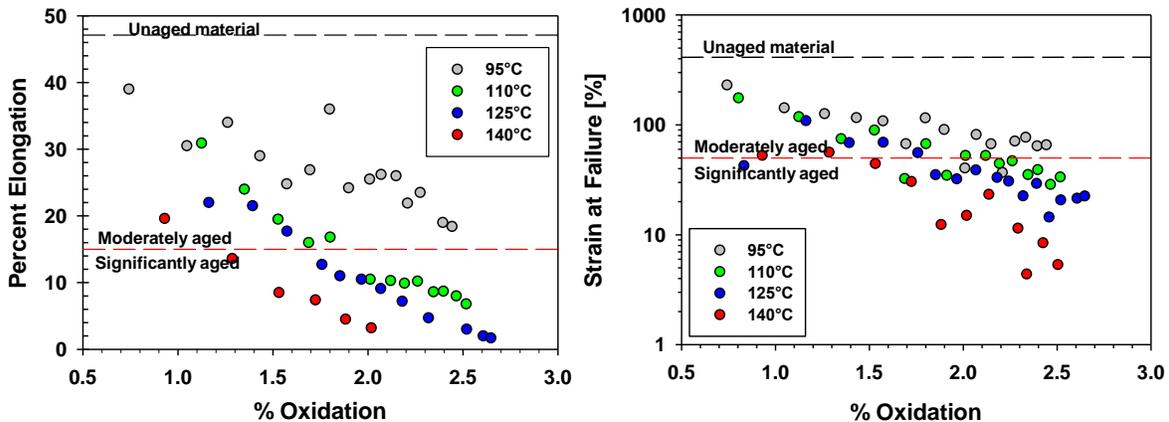


- Carbonyl level increases with aging exposure
- Thermo-oxidation drives degradation at elevated temperature
- Carbonyl increase to 0.02 absorbance units indicates significant oxidation

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Cross-correlation - chemistry and mechanical

- Oxidation drives material hardening and changes in mechanical properties.
- Oxidation rates allow oxidation levels to be estimated for accelerated aging.
- Thermo-oxidative aging often has good correlations between oxidation level and other property changes, but clearly some temperature dependence between oxidation and mechanical properties was observed.
- Note: These correlations are obtained for ox-rates declining with time.

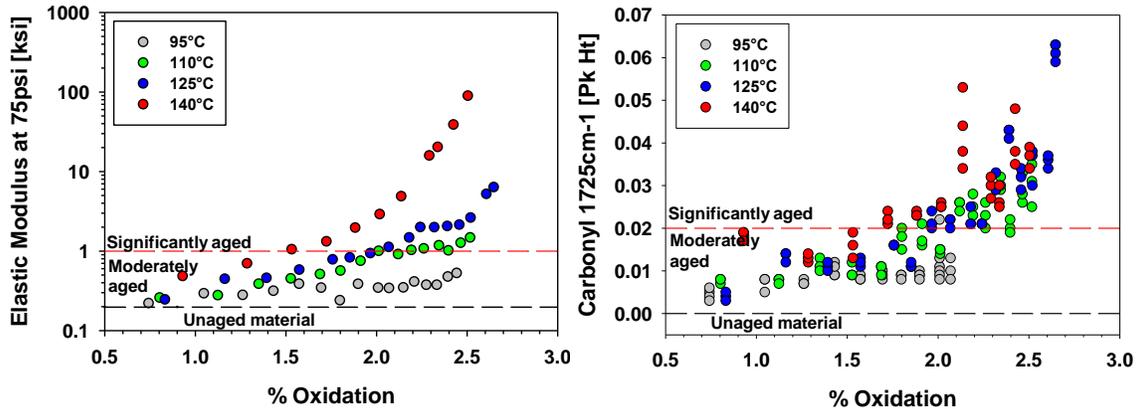


- Cross-correlations between projected oxidation levels, elastic elongation and elongation at break can be obtained
- It appears the material can accommodate more oxidation at lower T before properties change, but 2% oxidation generally affects other properties

16

Cross-correlation - chemistry and mechanical

- Oxidation drives material hardening and changes in mechanical properties.
- Oxidation rates allow oxidation levels to be estimated for accelerated aging.
- Thermo-oxidative aging often has good correlations between oxidation level and other property changes, but clearly some temperature dependence between oxidation and mechanical properties was observed.
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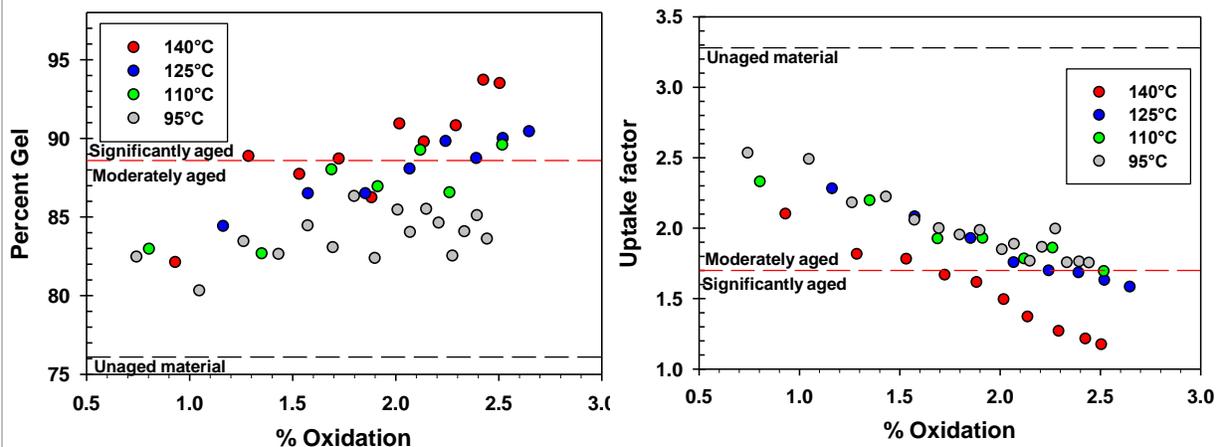


- Cross-correlations between projected oxidation levels, elastic modulus and carbonyl index
- It appears the material can accommodate more oxidation at lower T before properties change, but 2% oxidation generally affects other properties

17

Cross-correlation - chemistry and polymer network

- Oxidation drives material hardening and changes in mechanical properties.
- Oxidation should also be the dominant driver for polymer network changes in gel content and uptake factor. However, we observe scatter and some temperature dependency.

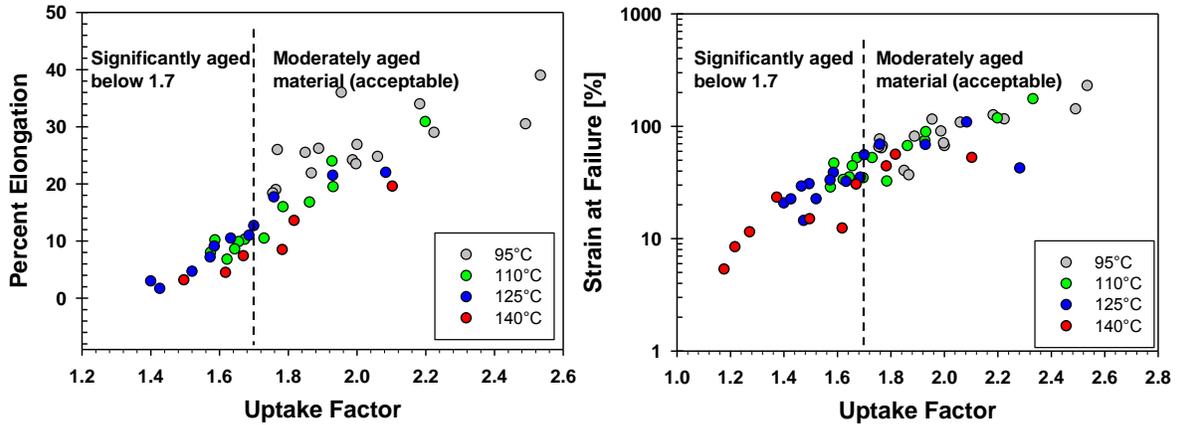


- Cross-correlations between projected oxidation levels and gel content or uptake factor are possible, but it appears the material can accommodate more oxidation at lower T before properties change

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Cross-correlation - polymer network and mechanical

- Polymer network changes usually affect elastic behavior and tensile elongation. A good cross-correlation should be observed.

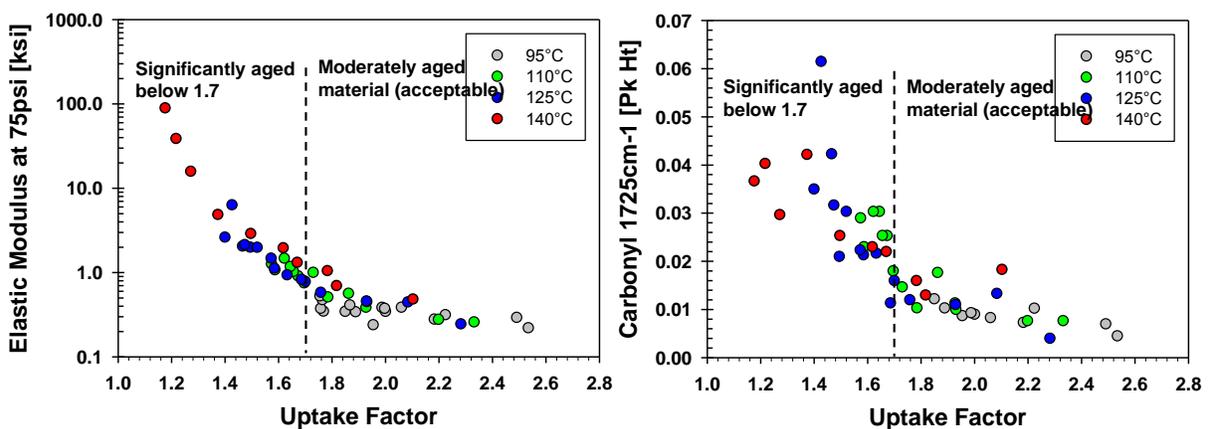


- Cross-correlation between uptake factor and elastic properties shows an underlying coupled degradation mechanistic pathway

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Cross-correlation - polymer network and mechanical

- Polymer network changes usually also affect modulus and are coupled with degradation chemistry (carbonyl level). Cross-correlation should be observed.

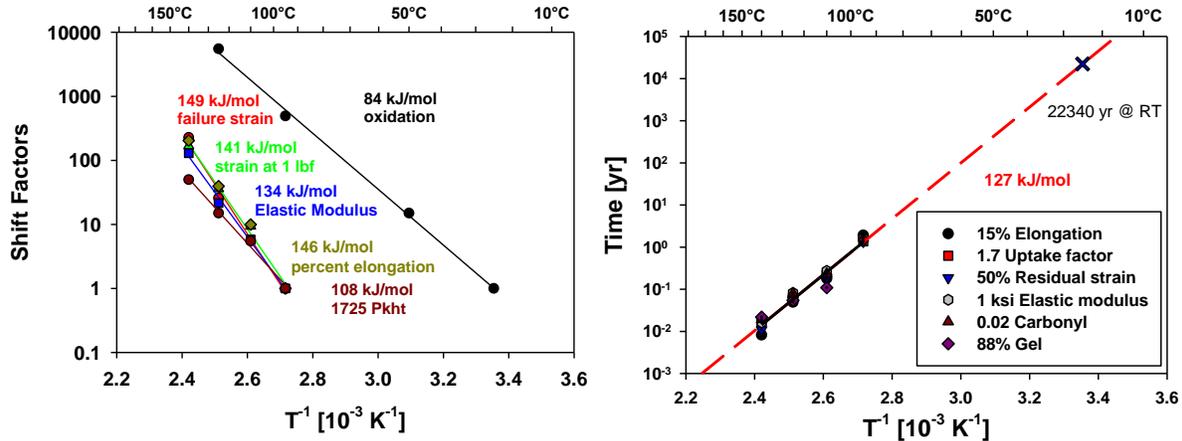


- Cross-correlation between uptake factor and modulus, and carbonyl level shows that network changes are mechanistically coupled with oxidation (carbonyl) and material hardness (modulus)

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Performance projections

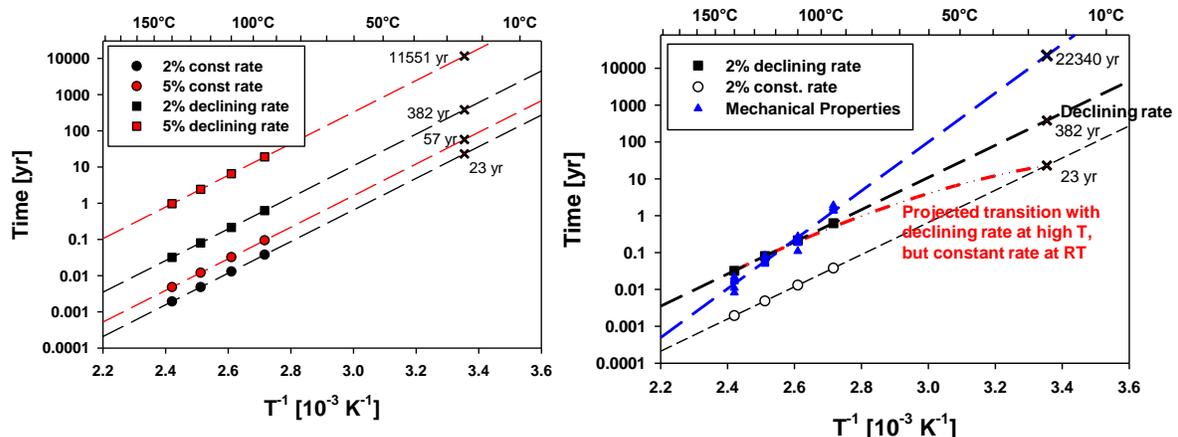
- Accelerated aging studies at 95 to 140°C have generated data as time to critical property changes (aging threshold in modulus, max elongation, elastic elongation, gel content, uptake factor and carbonyl level).
- These time data are summarized in an Arrhenius plot and can be extrapolated.



- Linear Arrhenius projections suggest significant lifetimes for this material due to the high activation energies determined between 95 and 140°C
- However, oxidation rates have a lower activation energy of ~84 kJ/mol
- All accelerated aging data suggest slow aging at RT, but is this realistic?

Projections of oxidation level

- A steady rate of $\sim 1e-12$ mol/g/s implies $\sim 2\%$ oxidation over 20 years.
- The field retrieved material, however has not shown significant oxidation.
- This suggest that oxidation rates at RT will indeed decrease over time.
- Projected times to 2% oxidation are compared with projected significant changes in average mechanical property changes, uptake factor or carbonyl level.
- A disconnect in Arrhenius plot between oxidation behavior (rates) and material property changes is apparent. This means fully consistent performance predictions can't be provided, but rates usually give better guidance.

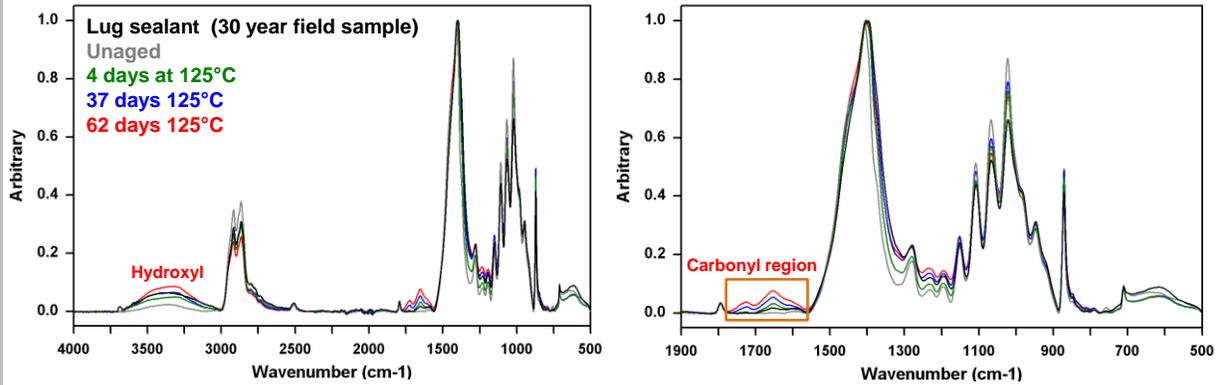


- Extrapolation of oxidation rates and oxidation levels suggest shorter lifetimes, with little margins at lower temperatures should a constant RT oxidation rate prevail

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Rating of field returned material – IR analysis

- The oxidation extent of field returned material can be rated by comparing its carbonyl intensity to that of polysulfide from accelerated aging.
- Carbonyl levels grow during natural aging (oxidation) of this material.

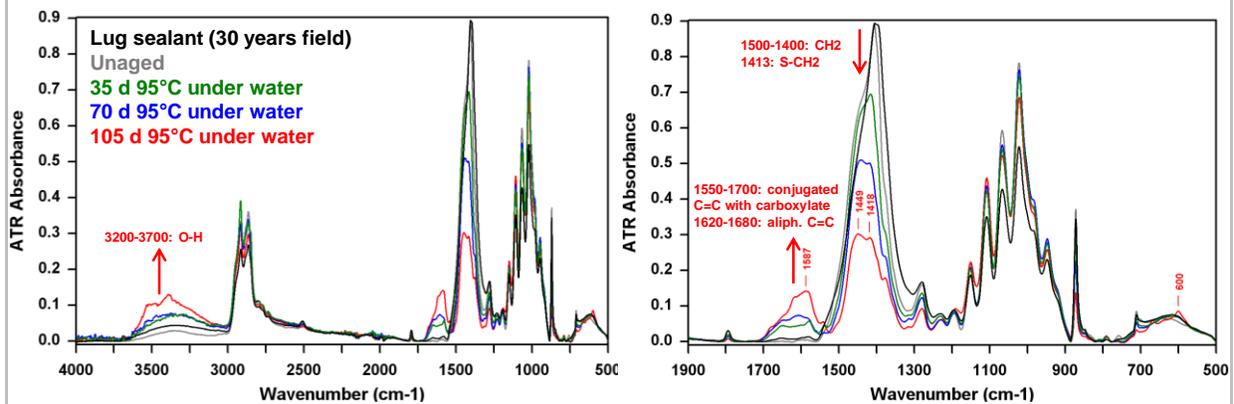


- Carbonyl intensity of field returned material is less than the equivalent of 4 d at 125°C, but hydroxyl is similar to 37 d at 125°C
- Field material has seen some oxidative aging

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Hydrolytic aging process – IR analysis

- Samples were immersed in water at 95°C for 35, 70 and 105 days
- IR suggests loss of CH₂ (1500-1400 cm⁻¹) and CH₂-S (scission) in parallel with growth in aliphatic C=C, likely conjugated with carboxylate. Significant hydroxyl growth consistent with carboxylate.
- Field returned material show neither loss in the CH₂ region nor an increase in the carboxylate implying that hydrolytic aging chemistry has not occurred.

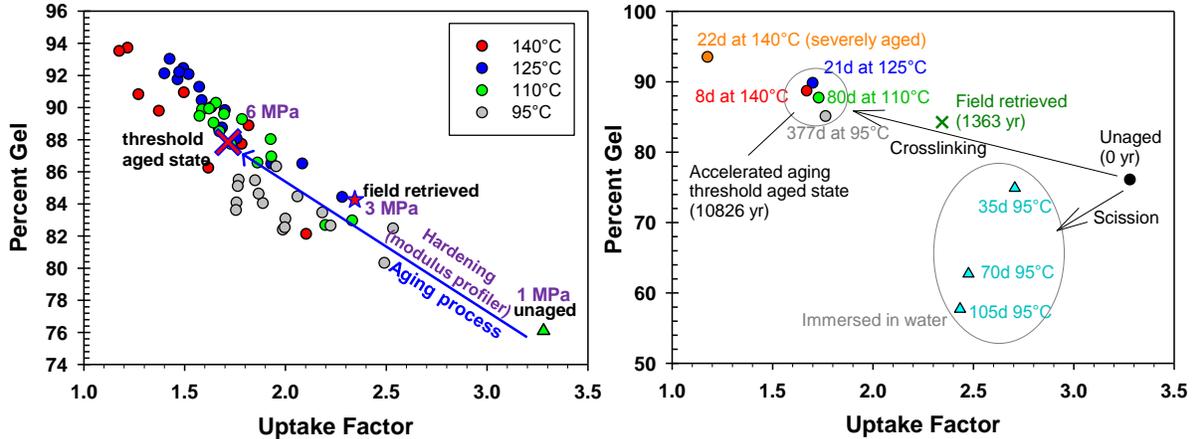


- Accelerated hydrolytic aging produces unsaturation, loss of CH₂-S linkage
- Field returned material does not show any IR signatures indicative of hydrolytic aging processes

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Rating of field returned material

- Only a few milligrams of field returned material (30 years in application) were available to determine uptake factor and gel content.
- Field returned material can be compared with uptake/gel data cross-correlated with threshold properties available from accelerated aging study
- Screening results for moisture induced aging can also be compared

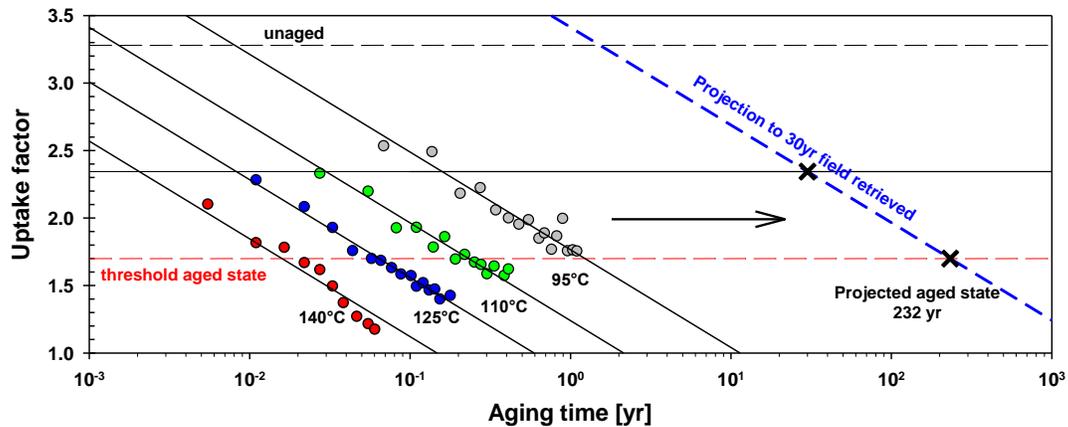


- The field returned material shows thermal aging as crosslinking
- Field material has not yet reached threshold property states
- Threshold is at 6.9 MPa tensile modulus, unaged at 1.4 MPa
- Modulus profiler yields 1.0 MPa for unaged and 3 MPa for field retrieved

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Projected behavior of field returned material

- We assume similar behavior in the gel/uptake trends during accelerated and RT aging processes. This means a similar aging process, but with different speed.
- Instead of using a linear extrapolation (constant E_a) for a calculated shift factor at RT, we instead use the partial aging state of the field retrieved material and its age as a 'time-property' indicator. This allows to project the additional time required at RT to reach its 'threshold aged state' and hence offers a perspective of remaining performance margin.



- The field returned aged for 30 years would require another 200 years at RT to transition to a significantly aged state assuming a similar aging process occurs at RT as observed during accelerated aging.

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Summary

Accelerated aging study:

- Accelerated aging of new sealant was conducted between 95 and 140°C. The material oxidatively hardens with loss in elasticity.
- Crosslinking is evidenced by network property changes in gel and uptake factor.
- Gel/uptake change faster initially; this is evidenced on log scale with time.
- Accelerated aging yields a high E_a of ~ 140 kJ/mol for multiple property changes.
- High lifetimes are projected for 25°C, but linear Arrhenius behavior lacks validity.
- Screening for aging under water (very high humidity) shows scission is dominant.

Oxidation rates:

- Oxidation rates were measured between RT and 125°C and yield 84 kJ/mol.
- The difference in E_a 's means that oxidation chemistry is not perfectly coupled with mechanical property changes during accelerated aging, but significant property changes are associated with ~ 2% oxidation.
- Oxidation rates at 125 to 50°C decline over time, i.e. with oxidation level, but uncertainty exists whether this will also occur at RT.
- Performance projections can be made as time required to reach 2% oxidation levels with declining or constant rates (worst case at lower temperatures).

Field returned material:

- Only gel/uptake data could be obtained and crosslinking due to aging is apparent, but below the threshold of significant changes in mechanical properties. The material does not show the features of humidity induced scission related degradation.
- Based on its gel/uptake 'rating' between unaged and 'aged' state (threshold properties in this study) and its time dependence the material has aged about 1/3 over 30 years.
- Similar partial aging state below 'threshold level' is observed for elastic modulus.

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Conclusion and Recommendation

- Accelerated aging study suggests material would perform easily for another 30 years at RT, but the extensive linear extrapolation is of course questionable.
- Oxidation rates decline with time at high temperature and if assumed this behavior also occurs at RT, critical oxidation levels as a performance indicator then also suggest sufficient performance margin for another 30 years at RT.
- As worst case scenario, if the oxidation at RT remained steady ($9e-13$ mol/g-s) a 2% oxidation level associated with significant material changes is calculated for 23 years at RT. This would imply performance limits for reuse, however, this is clearly in conflict with the state of the field returned material, and also that the rate will likely decline at RT.
- Based on gel/uptake data and modulus trends the 30 year old retrieved material has not aged much within its absolute property change regime to reach an aged threshold, but the time dependence is not linear, and it is projected it would take an additional ~ 200 years to change from the retrieved state to 'aged' state.

Recommendation:

- Based on all the evidence obtained we believe that the sealant will have an additional 30 year performance margin, however, the usual uncertainties remain within extrapolations of any aging behavior.

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