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Polymer Oxidation and its Impact on Materials Performance and Lifetime Prediction

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Acknowledgements

Collaborators and co-workers at SNL
Angela Dayile, Adam Quintana, Nick Giron, Manny Rojo, Jim Aubert
(Former colleagues: Ken Gillen, Roger Assink, Roger Clough)

Organizing committee for MoDeSt
MoDeSt conference chair and staff: Jan Pilar

Examples from the literature, full credit is given to the original authors

Thank you and a warm welcome to all of you!

Goal: Provide an overview of the field and offer new researchers a broad perspective

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Thermal Oxidation of Polymers 101

Linking polymer chemistry and material science

- **WHY?** Intrinsic material properties: Polymer sensitivity to oxidation
  Initiation processes: What makes a material weak?
  Oxygen and hydrocarbons react as oxidizer – fuel

- **HOW?** Degradation mechanism: What is going on?
  Basic autoxidation scheme, free radical chemistry
  Temperature effects: accelerated degradation

- **WHERE?** Surface versus bulk degradation
  Damage distribution in a material
  Diffusion limited oxidation

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Thermal Oxidation of Polymers 101

Linking polymer chemistry and material science

- **WHAT it does it lead to?**
  - **Correlation of chemistry with other properties**
  - **Definition of performance requirements**
  - **Useful mechanical properties suffer**

- **WHEN?** **The universal question for all of us:**
  - **We must live with AGING**
  - **Nothing lasts forever, 2nd law of thermodynamics**

- **Lifetime prediction: How to extrapolate small changes?**
- **Even the best anti aging pill cannot provide eternal life**
- **The best antioxidants cannot make polymers last forever**

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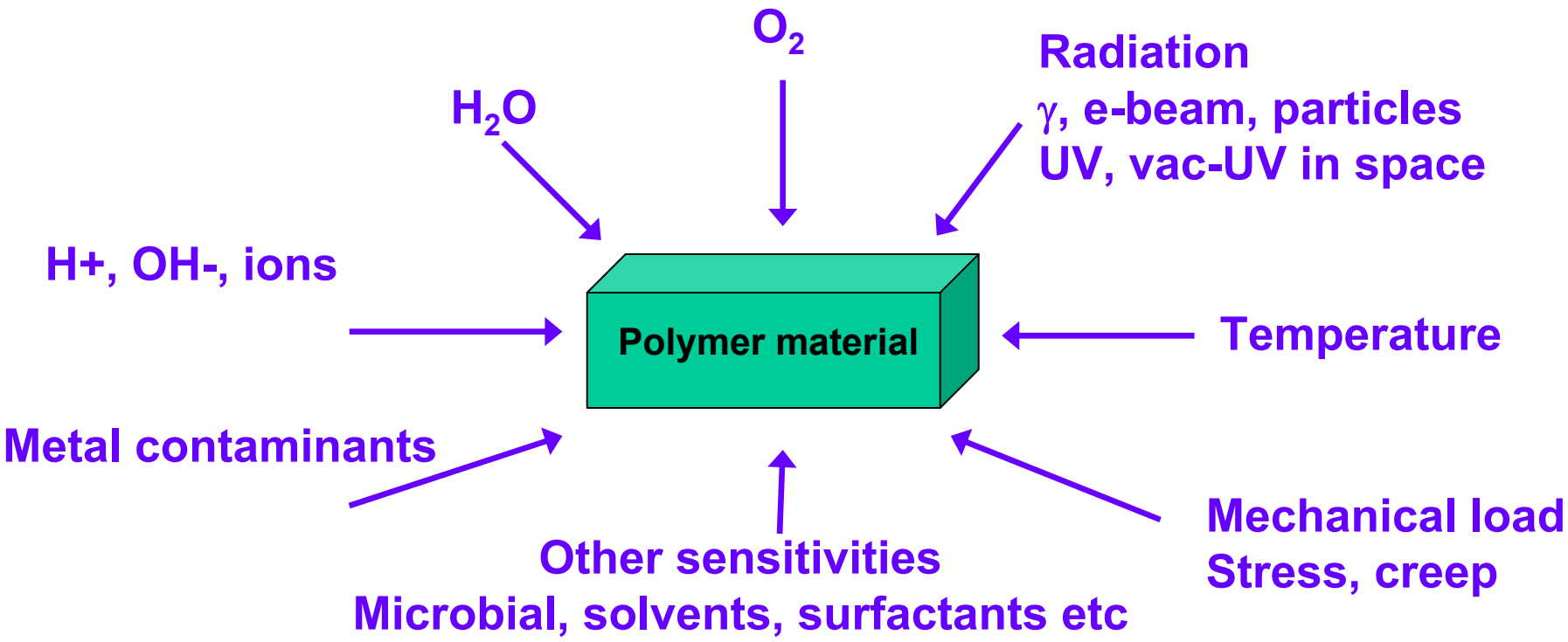
Why is Lifetime Prediction Complex?

- Polymers are exposed to a multitude of environments
- Materials often display particular sensitivities
- Combination of oxygen, temperature, hydrolysis, UV/radiation



Major differences between oxidative and inert conditions

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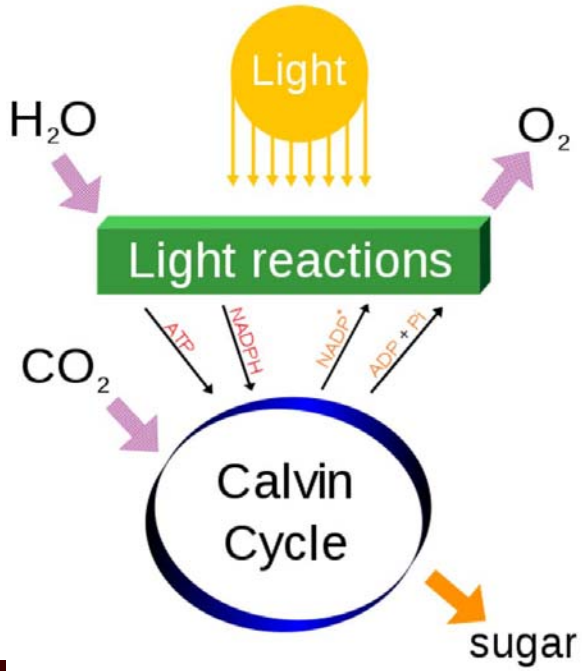
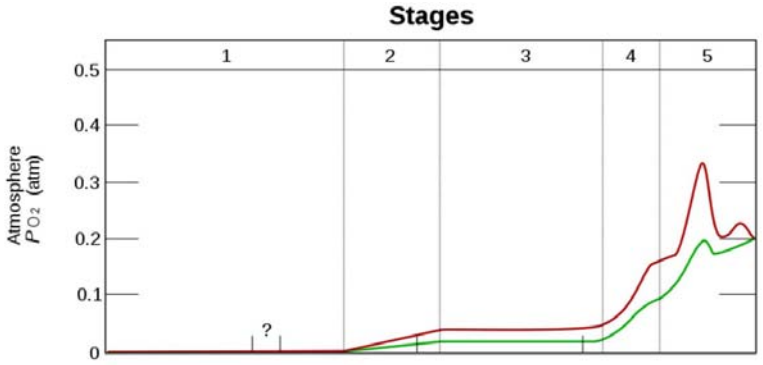
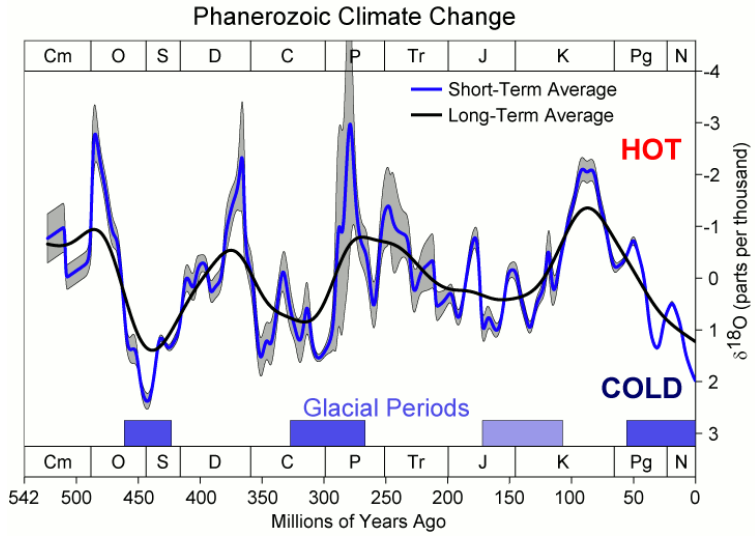
Why? Because there is Oxygen

- The third most abundant element
- Nature's photosynthesis CO_2 reduction byproduct
- Each year 0.05% of the atmosphere recycled in carbon cycle

Spectral lines of oxygen







Hydrocarbon polymers are part of the carbon cycle

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Why? Because Oxygen is Aggressive

- Fast redox reactions - Slow rust for metals
- Rapid combustion - Slow degradation for polymers

Oxidation of Al/Mg

Rapid pseudo-monomer oxidation

Degraded polymers during thermal aging

Oxygen attacks polymers – just a matter of time

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Why? Slow Combustion

- Thermal degradation of polymers is normally without flames
- But the underlying oxidation process is similar

Aging ovens
We select suitable temperature depending on polymers

Pyrolysis
Volatiles

Rapid oxidation of cellulose/lignin

Oxidation rate increases with T →

Oxidative thermal degradation is slow combustion without a flame
From hydrocarbons to CO_2 and H_2O

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How - Where? Depends on Depth

- What is oxygen availability?
- What is the O_2 concentration in a polymer?

Biopolymer oxidation depends on elevation

Burning glucose on Mt. Everest

In the deep too much O_2 is toxic

Depends on partial pressure

Same issues for polymers:
P_{O2} and S_{O2} (O_2 partial pressure and solubility)
Material oxidation depends on depth
Surface is often more oxidized
Oxygen will attack polymers – just a matter of TIME AND DEPTH

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Question: Imagine you work as the editor for PDST; would you worry about your job?

- 60 years of polymer aging and we have learned a lot!
- We know how to make polymers degrade!
- We can meet every year to discuss trends, MoDeSt and PDDG

- Photodegradation – higher dose rates and higher T
- Hydrolysis – stronger acids and higher T

- How do we accelerate thermal oxidation?
- O_2 availability – increase pressure
- Oxidation reaction – increased temperature – pyrolysis
- (Probably more than 50% of papers to PDST have TGA data!)

YES: Polymer Degradation is Easy to Achieve

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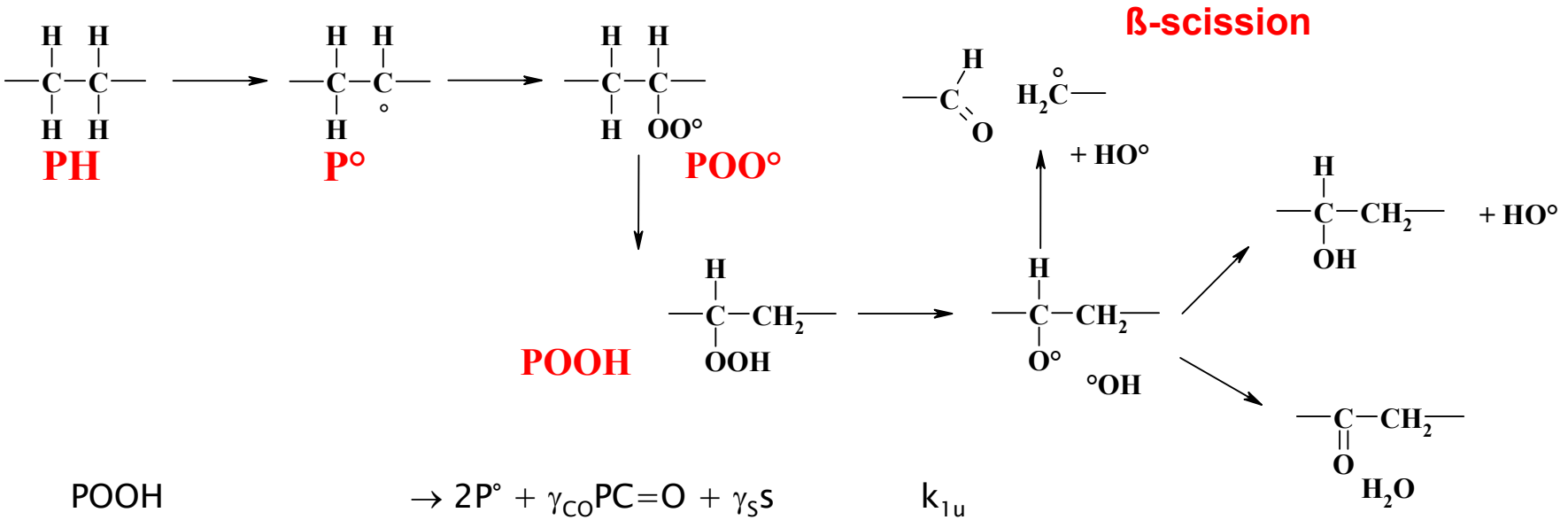
Free Radical Autoxidation Mechanism

- Polymer oxidation – Basic Auto-oxidation Scheme (BAS)
- Hydrocarbon oxidation in the 1950s, Bolland, Bateman and Gee



POOH	$\rightarrow 2P^{\circ} + \gamma_{CO}PC{=}O + \gamma_{S}S$	k_{1u}
$P^{\circ} + O_2$	$\rightarrow POO\cdot$	k_2
$POO^{\circ} + PH$	$\rightarrow POOH + P^{\circ}$	k_3
$POO^{\circ} + POO^{\circ}$	$\rightarrow$ Inactive products $+ O_2$	k_6

Polymer chain cleavage and oxidation

Hydrocarbon, peroxides, free radicals, scission, crosslinking, H-abstraction/transfer, carbonyls, aldehyds, alcohols, CO_2, H_2O

Gillen KT, Wise J, Clough RL. . *Polym Degrad Stab* 1995;47:149
Verdu S, Verdu J. *Macromolecules* 1997;30:2262
Colin X, Fayolle B, Audouin L, Verdu J. *Int. J. Chem. Kinetics* 2006;38:666.

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Mechanism – Kinetic Modeling

- **Combinations of differential equations**
- **Modeling of experimental data, extraction of rate constants, Ea and development of predictive oxidation models**

$POOH \rightarrow 2P\bullet$	(k_{1u})	$P\bullet + P\bullet \rightarrow ....$ (k_4)
$2POOH \rightarrow P\bullet + PO_2\bullet$	(k_{1b})	$P\bullet + PO_2\bullet \rightarrow \ldots$ (k_5)
$P\bullet + O_2 \rightarrow PO_2\bullet$	(k_2)	$PO_2\bullet + AH \rightarrow ....$ (k_{s1})
$PO_2\bullet + PH \rightarrow POOH + P\bullet$	(k_3)	$PO_2\bullet + A\bullet \rightarrow \ldots$ (k_{s2})
$PO_2\bullet + PO_2\bullet \rightarrow \ldots$	(k_6)	

$$\frac{d[P\bullet]}{dt} = 2k_{1u}[POOH] + k_{1b}[POOH]^2 - k_2[P\bullet][O_2] + k_3[POO\bullet][PH] - 2k_4[P\bullet]^2 - k_5[P\bullet][POO\bullet]$$

$$\frac{d[POOH]}{dt} = -k_{1u}[POOH] - 2k_{1b}[POOH]^2 + k_3[POO\bullet][PH]$$

$$\frac{d[POO\bullet]}{dt} = k_{1b}[POOH]^2 + k_2[P\bullet][O_2] - k_3[POO\bullet][PH] - k_5[P\bullet][POO\bullet] - 2k_6[POO\bullet]^2$$

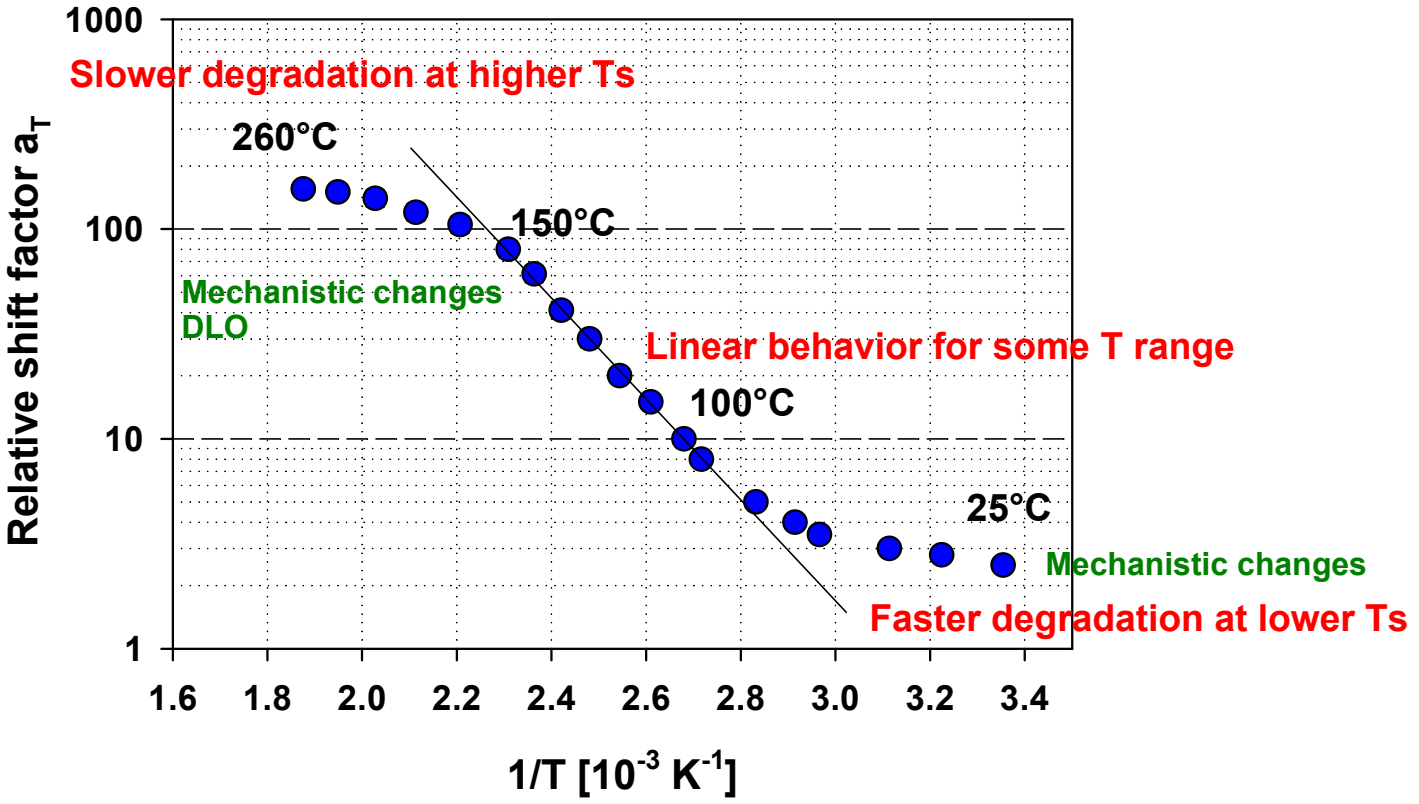
$$\frac{d[PH]}{dt} = -k_{1u}[POOH] - k_{1b}[POOH]^2 - k_3[POO\bullet][PH]$$

$$\frac{\partial[O_2]}{\partial t} = D_{O_2}\frac{\partial^2[O_2]}{\partial x^2} - k_2[O_2][P\bullet] + k_6[PO_2\bullet]^2$$

Many papers, > 15 years by the ENSAM group, Verdu, Audouin, Fayolle, Colin and Richaud, also Gillen (SNL)

Accelerated Aging – Lifetime Prediction

Most accelerated aging studies use a convenient temperature range



Anomalies for lower T degradation are well-known
High T deviations are less of an issue, no need to test faster than days, unless we consider OIT and rapid DSC approaches

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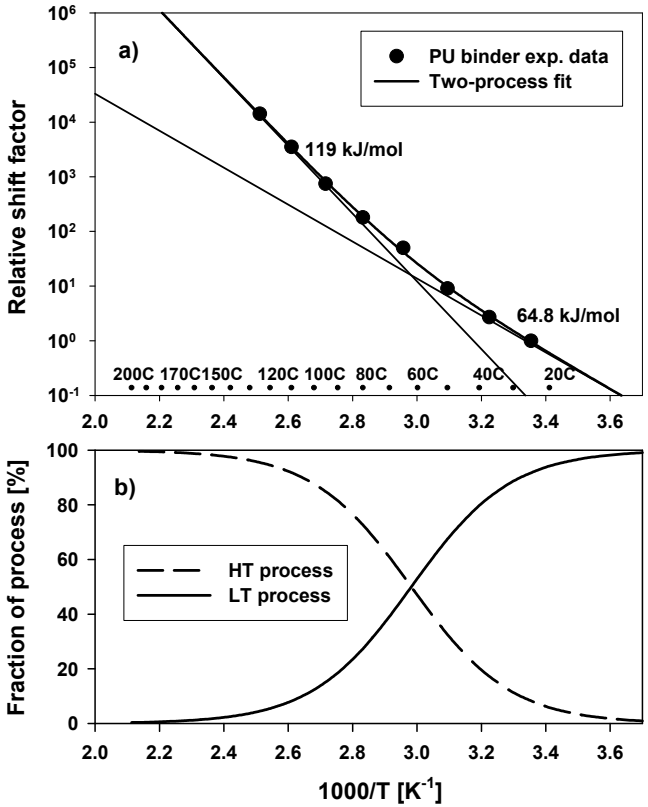
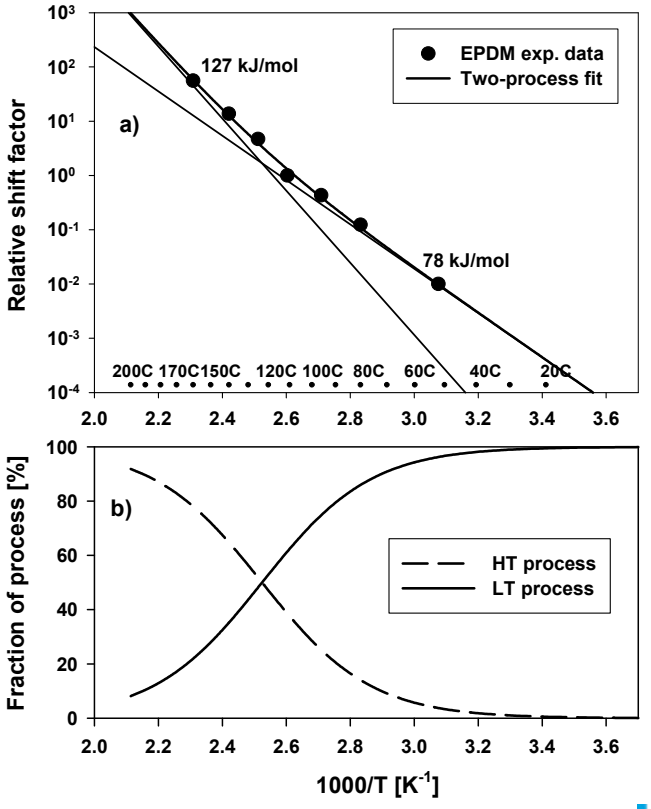
Curvature in Arrhenius Plots

- Without refined kinetic models, a two-process behavior
- Combination of high and low temperature process
- Evidence for curvature in many materials
- Important for lifetime predictions

$$k_{sum} = k_1 + k_2 = A_1 * \exp(\frac{E_{a1}}{RT}) + A_2 * \exp(\frac{E_{a2}}{RT})$$





M. Celina, K. Gillen, R. Assink, *Poly. Deg. Stab., 90* (2005) 395

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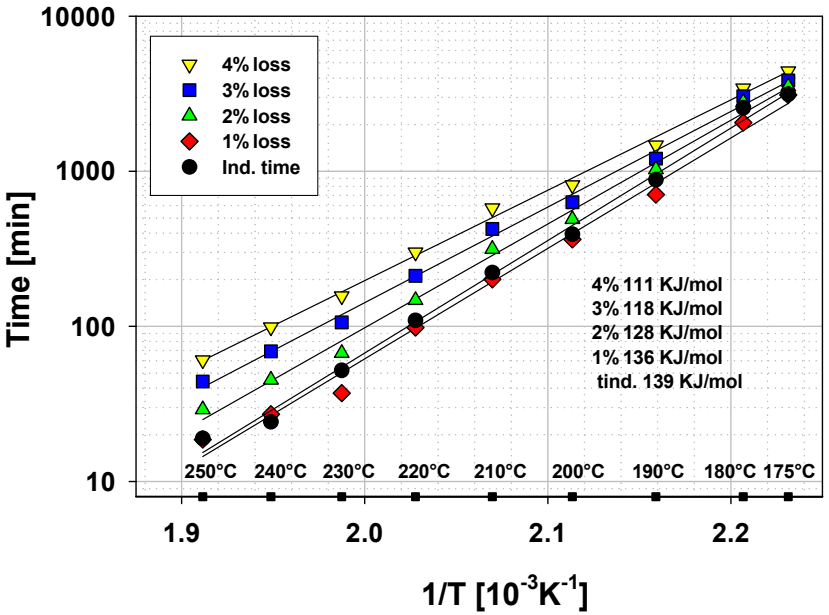
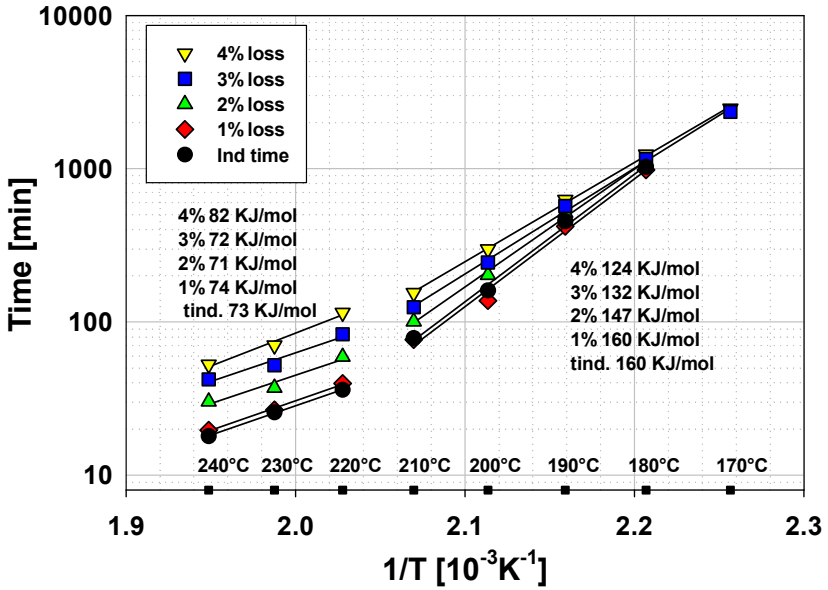
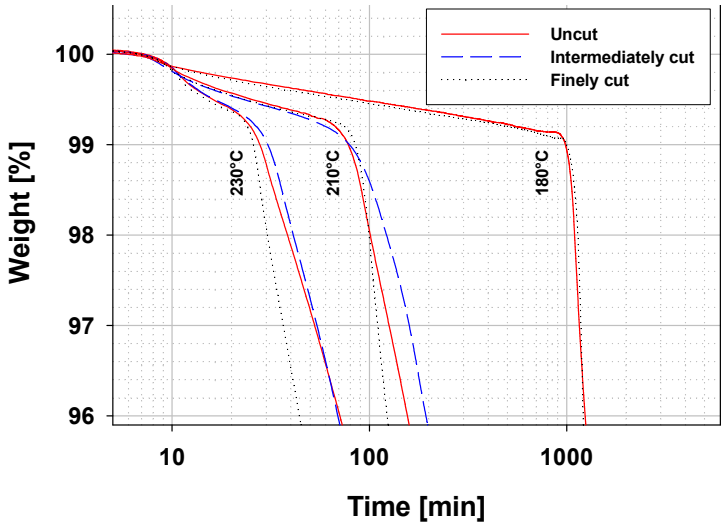
High T fast Oxidative Aging

Example of EPDM elstomer material under Air and Oxygen in TGA





- Arrhenius curvature at high temperatures
- TGA weight loss behavior depends on shape of sample and surface area, cut specimens
- Many numbers are available
- Endless papers of TGA and polymers
- Mathematical approaches, Osawa etc.

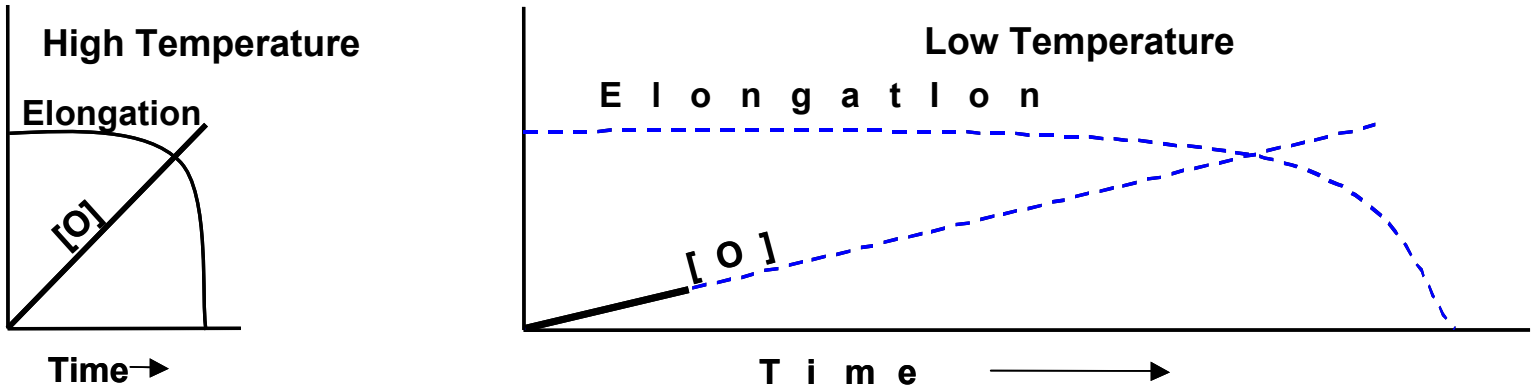


SR

Oxuptake Correlation
Oxidative State and Mechanical Property

The method depends on:

1. **Close relationship between [O] and properties**
2. **Linear or "well behaved" [O] consumption**



Measuring a small change in a chemical property rather than a small change in a mechanical property

J. Wise, K. Gillen, R. Clough, *Poly. Deg. Stab., 49* (1995) 403

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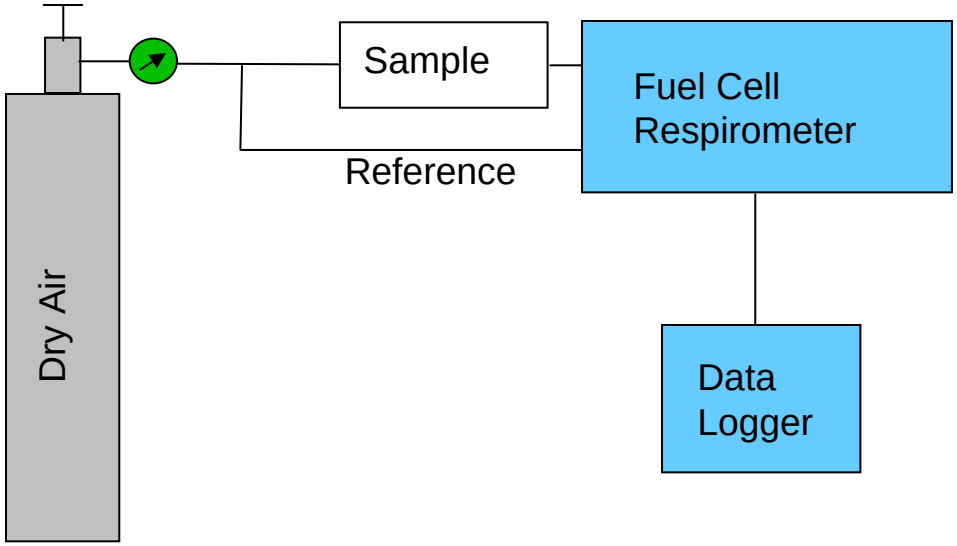
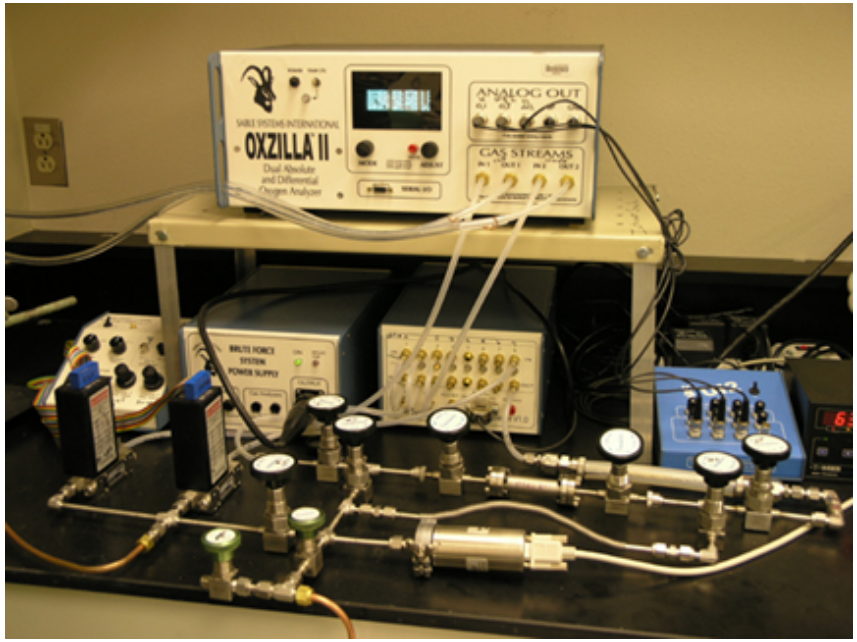
Respirometer used to Measure Extremely Slow Oxidation Rates in Polymers





- **Commercial respirometer based on differential fuel cells, used by the biological community.**
- **High sensitivity and rapid repeat analyses**
- **Effective sample handling**
- **More attractive than GC oxuptake approaches, but does not measure CO2**

R. Assink, M. Celina, J. Skutnik, D. Harris, *Polymer, 46* (2005) 11648

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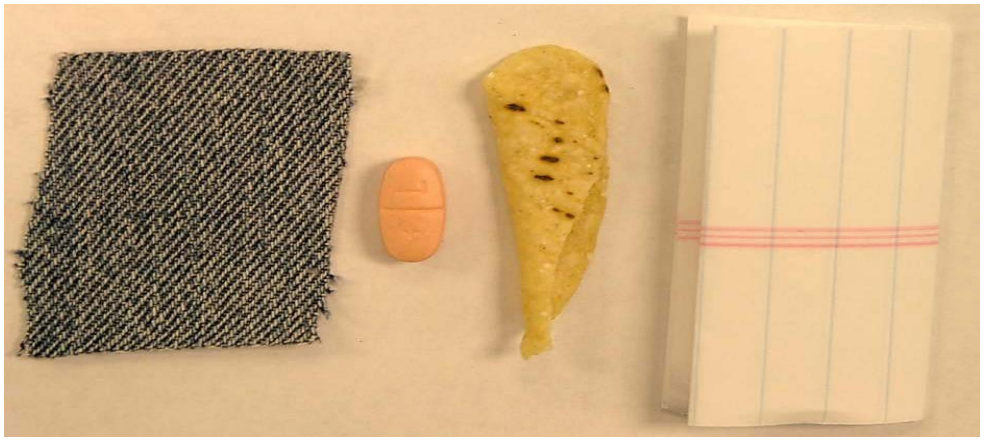
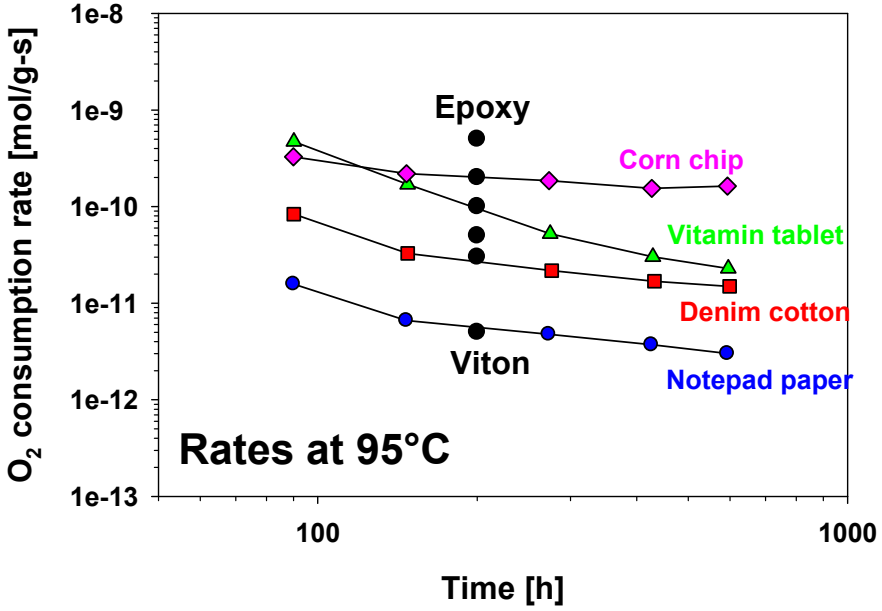
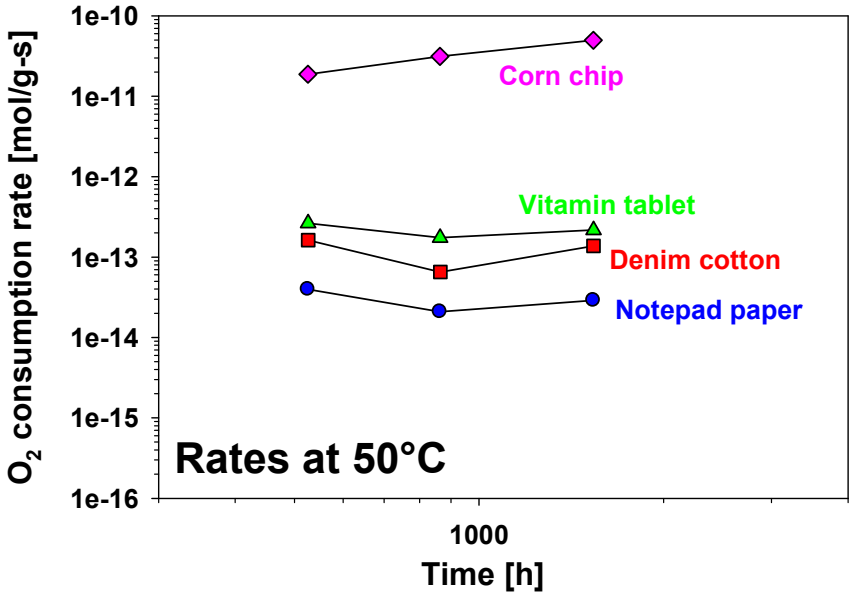
Natural Polymers and Oxidation



Cotton
Vitamin tablet
Corn chip
Paper





These materials fall within the range of other polymers

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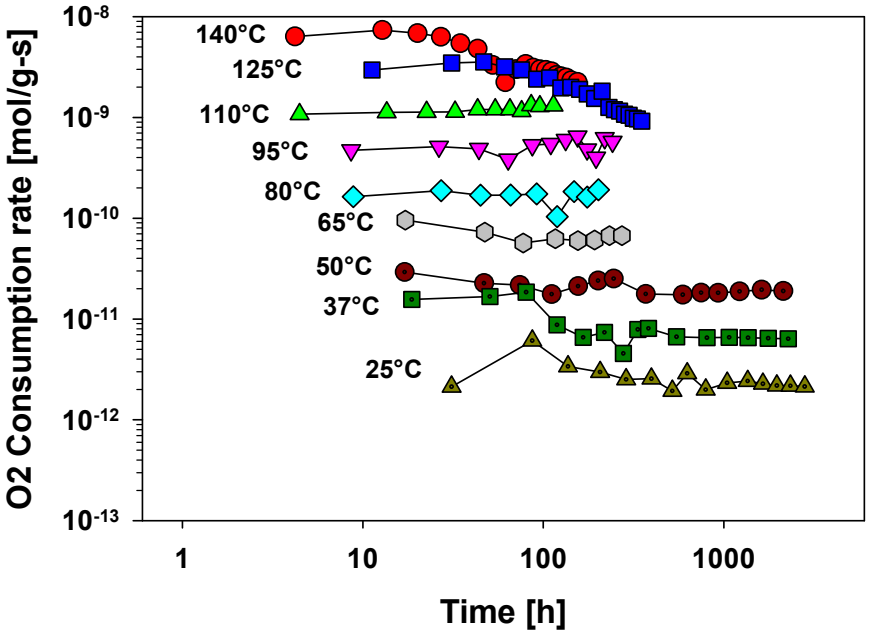
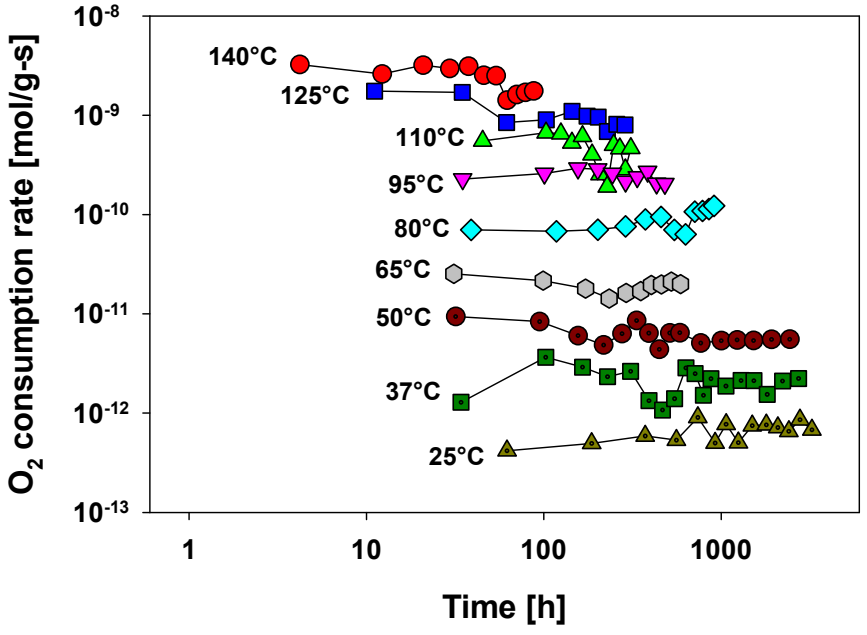
Epoxy Materials and Oxidation

Epon 828 – Ancamine 2049
(cyclohexyl aliphatic diamine)



Epon 828 – Jeffamine D230
(polypropylene ether amine)



- **Ground breaking work, unexpectedly high reactivity**
- **For the first time we have obtained intrinsic oxidation rates for two epoxy materials at 25-140°C**

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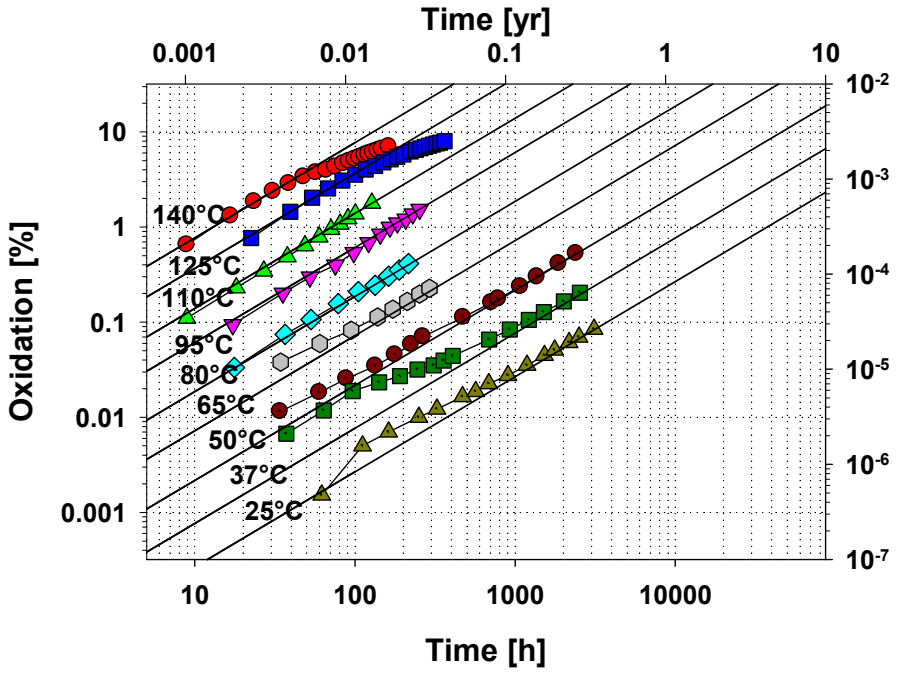
Epoxy Materials and Oxidation

Epon 828 – Ancamine 2049
(cyclohexyl aliphatic diamine)



Epon 828 – Jeffamine D230
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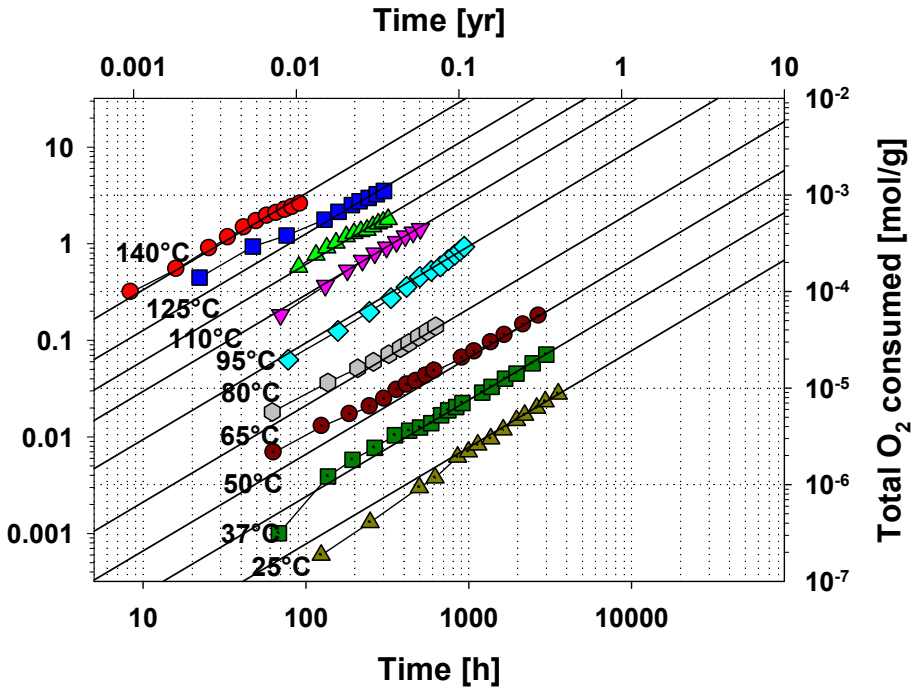

Fast oxidation rates in comparison with other materials

A2049 2% oxid. 125°C=2.3d 110°C ~6d, 80°C=45d, 50°C=384d, RT=8.5y
D230 2% oxid. 125°C=6.5d 110°C ~14d, 80°C=88d, 50°C=3.5y, RT=29y
A2049 20y at 50°C ~ 38%, 20y at RT ~4.7%,
D230 20y at 50°C ~ 11.6%, 20y at RT ~1.4%

Epoxies will oxidize over extended times and at elevated T

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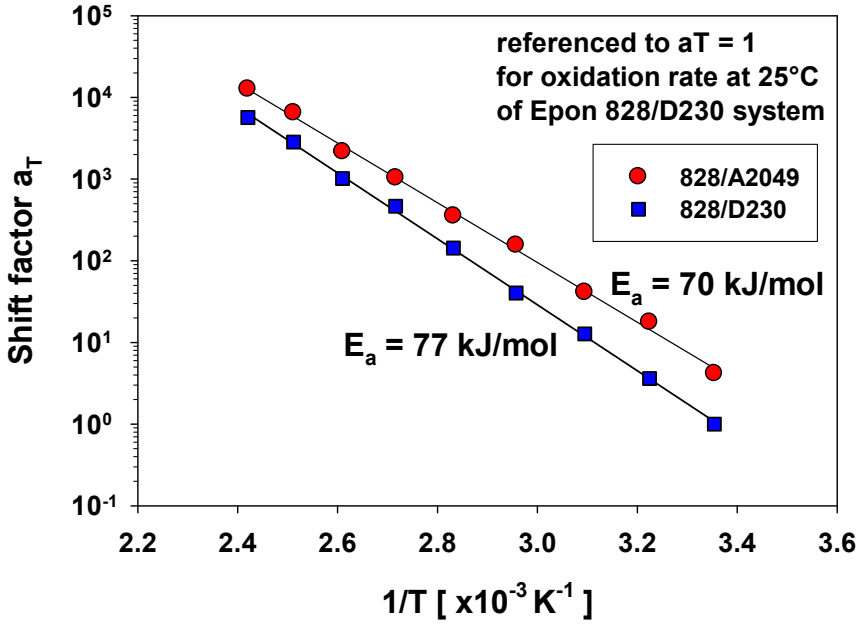
Epoxy Materials and Oxidation

- Nice linear Arrhenius plots
- Little variation in Ea, around 70 to 80 KJ/mol
- Interestingly, the aliphatic amine epoxy system oxidizes faster than the polyether amine system



Normalized rate comparison

Extrapolation to 5% oxidation at 180°C yields:
828/A2049 ~ 11.4h hours, 828/D230 ~ 20.4h

Composites at high temperatures will oxidize quickly

Numerous papers by ENSAM researchers on high T composite material degradation and DLO (Colin, X)

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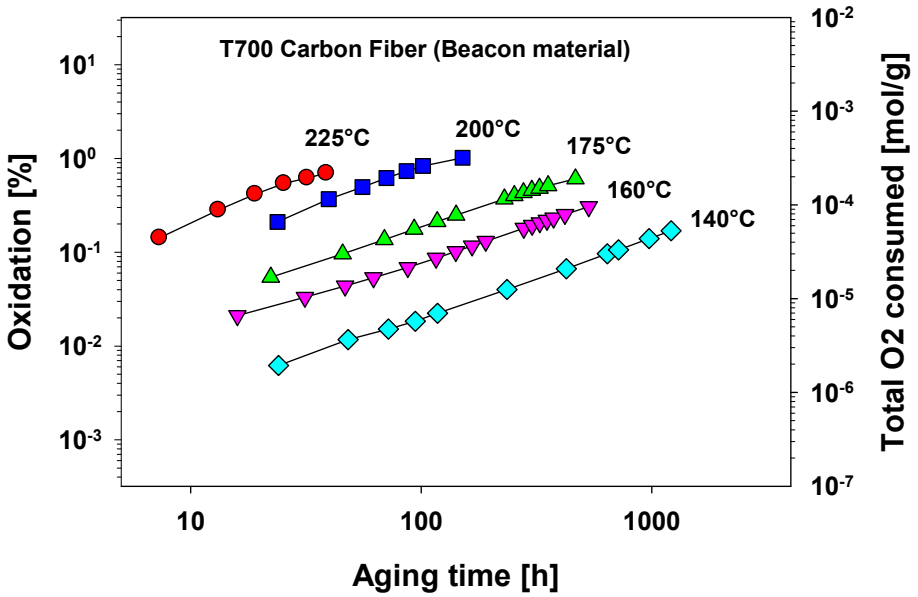
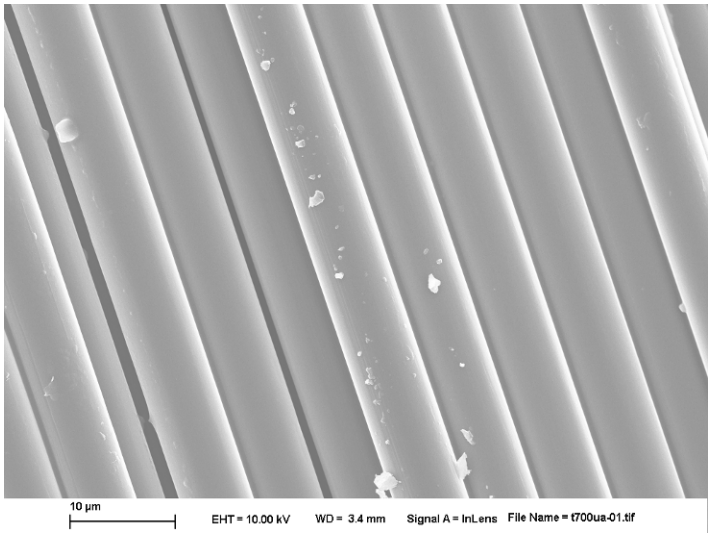
Carbon Fiber used in Composites

Idea: Use atmospheric oxygen to induce thermal carbon oxidation
Explore if oxidation can modify the surface or just produces CO_2
Can we measure thermal oxidation rates of carbon?
How does carbon oxidize at moderate temperatures?





T700 Carbon Fiber, Unaged

Achieved controlled oxidation of carbon fiber under air in ampoules
Measured oxidation rate and oxidation with consecutive exposure

Carbon fibers oxidize at moderate temperatures and it can be measured

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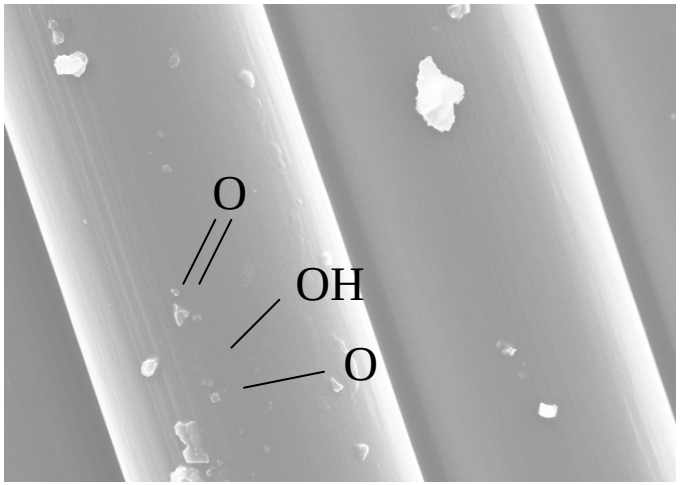
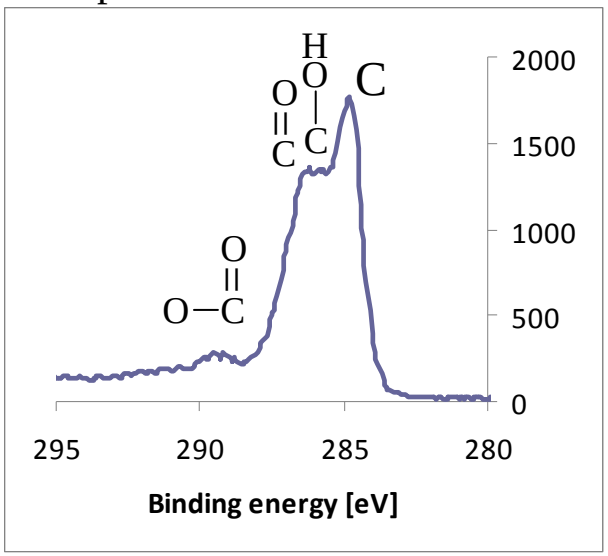
Carbon Fiber used in Composites



T700 Carbon Fiber, Unaged

XPS to probe surface oxidation of carbon



Controlled oxidation of T700 carbon fiber under air

Temp [°C]	Time [h]	% oxidation (GC)	O2 liberated as CO2 and CO
160	360	0.25%	76%
175	120	0.275%	74%
200	20	0.36%	71%

Thermal treatment to achieve oxidative modification

75% of O_2 that attacks the carbon is liberated as CO_2 and CO

Need to understand the resulting carbon surface modification

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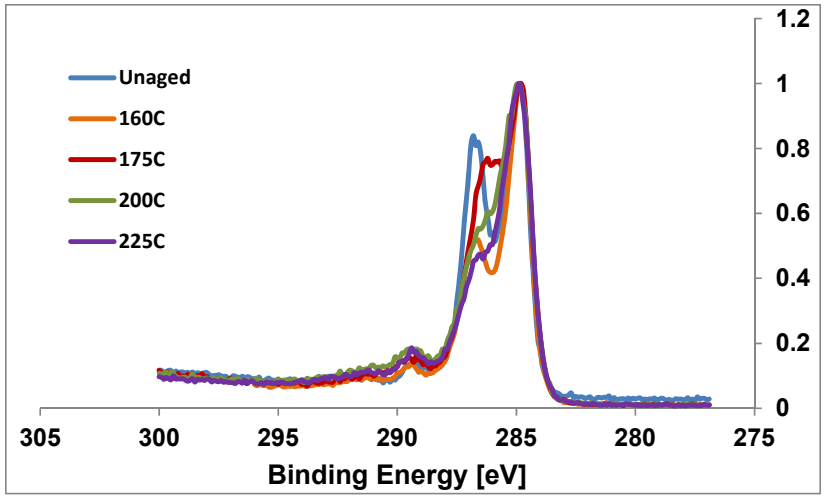
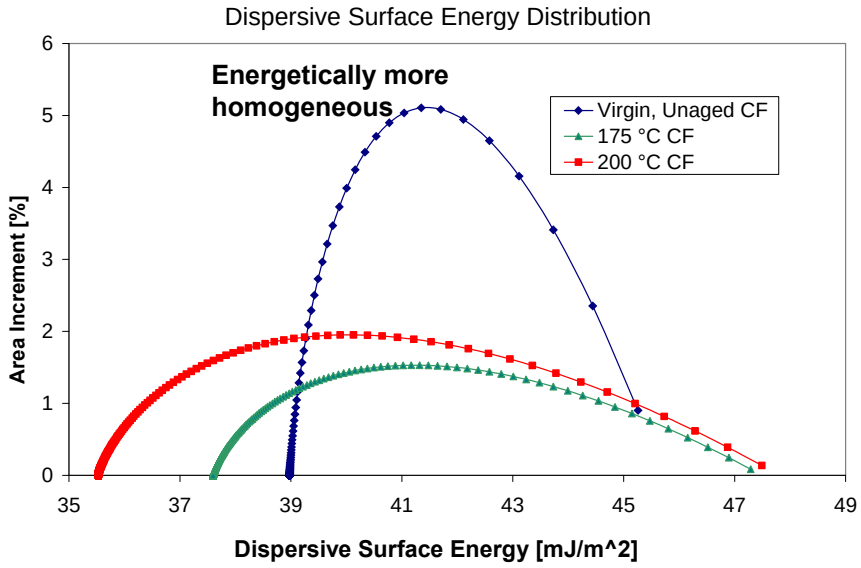
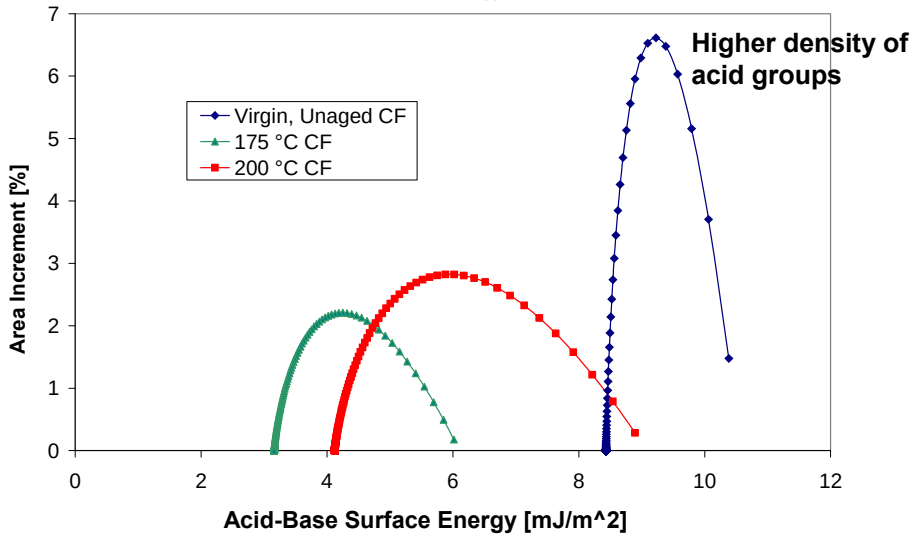
Carbon Fiber used in Composites





- Oxidation of carbon surface does not result in extra surface roughening
- Interestingly, the oxidation process results in surface ablation
- Original fiber has high degree of oxidation species



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O_2 Partial Pressure Affects oxid. Rate

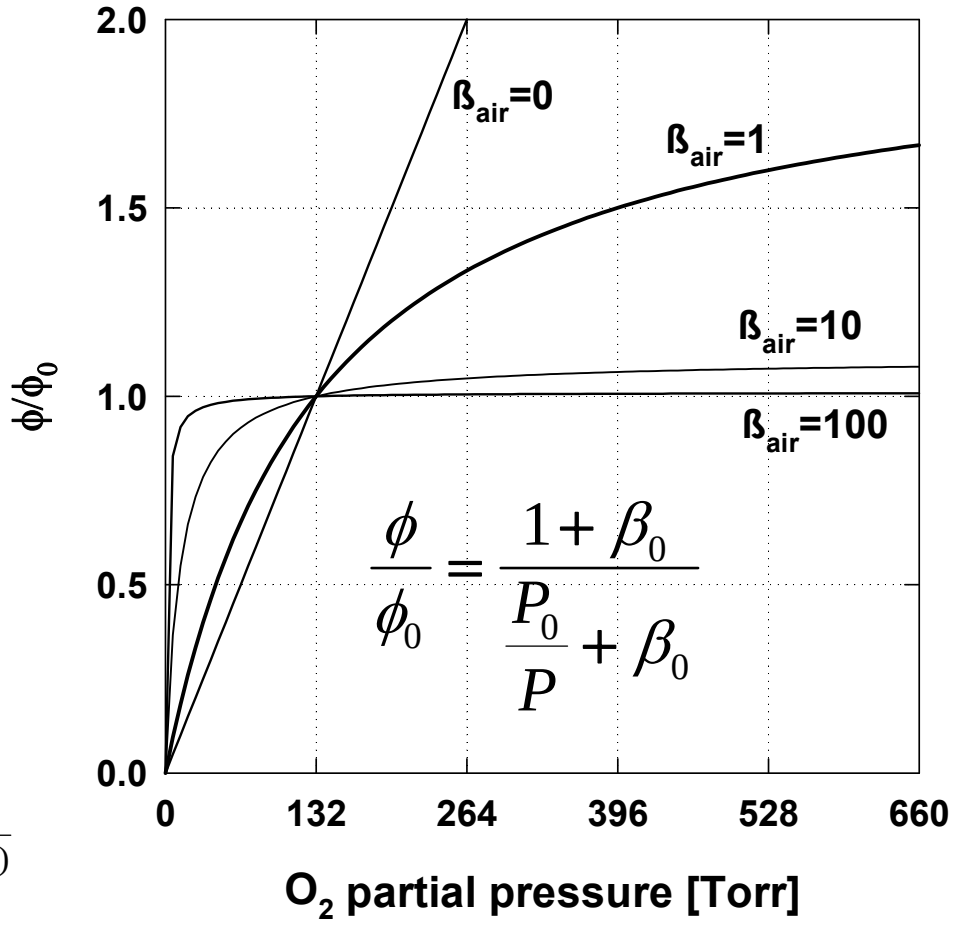
- Beta factor ($ß_0$) is used to correlate oxidation rate and partial pressure
- $ß_0$ is a material property, but can depend on T
- $ß_0$ involves rate constants from basic autoxidation scheme

$$\beta_0 = f(C_2, [O_2]) = C_2 * S * (p_{O_2})_0$$

$$\beta = \beta_0 * \frac{P_{O_2}}{(P_{O_2})_0}$$

$$C_{1b} = k_2\left(\frac{R_i}{2k_4}\right)^{1/2} \quad C_{2b} = \frac{k_2}{k_3}\left(\frac{k_6}{k_4}\right)^{1/2}$$

$$C_{1u} = \frac{k_2 R_i}{k_8} \quad C_{2u} = \frac{k_2 k_7}{k_8(k_3 + k_7)}$$



- The description of polymer oxidation involves physical chemistry
- Very important to predict degradation profiles

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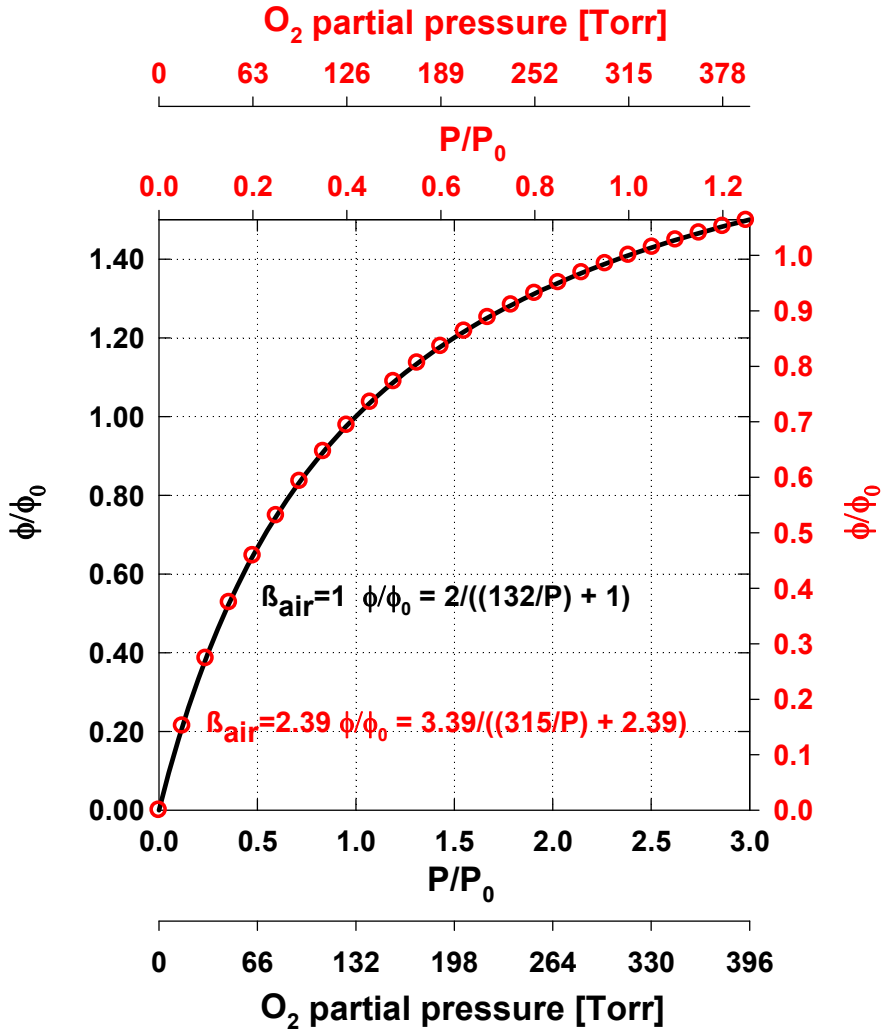
O_2 Partial Pressure Affects oxid. Rate

- $ß_0$ allows predictions of rate for various pressures
- For $ß_0 = 1$
- For ABQ, O_2 vs air, f=1.65
- ABQ, $P_{O2} = 132$ Torr
- Sea level, $P_{O2} = 160$ Torr
- Sea level 10% faster

- Oxygen Induction time (OIT)
- Air vs O_2 atmosphere
- Accelerates stabilizer reaction differently than polymer oxidation (different $ß_0$)
- When DLO applies, the polymer becomes sensitive to P_{O2}



- One fundamental rate dependency on partial pressure
- Polymer aging is different at sea level or in the mountains

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Warning:
To visualize DLO the animal used in the production of the next slide has been hurt

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DLO Conditions in Polymer Aging
Example: Char on the BBQ

Aging of protein elastomers

Hot BBQ
"Can't wait"

Heterogeneous, like DLO aged

Patience will lead to a homogeneous "well-done"

Differences in perceived taste and performance

BORED at the next BBQ? Think about DLO

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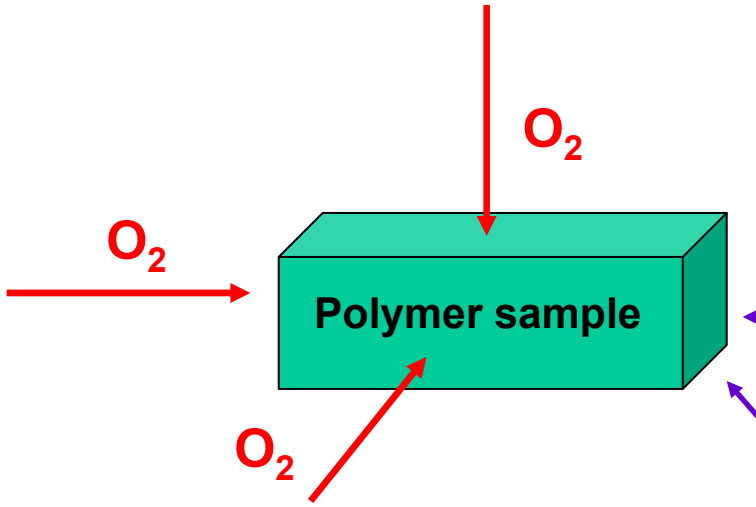
DLO Develops for Severely Accelerated Conditions



Stress variable	DLO conditions
Thermal	excessive T (frying pan)
UV	strong dose rate (sunburn)
radiation	high dose rate (e-beam, ion beam)

- Accelerated aging tests for polymers
- Differences between homogeneous oxidative, DLO and inert/vacuum
- Affects overall predictive value of experiments

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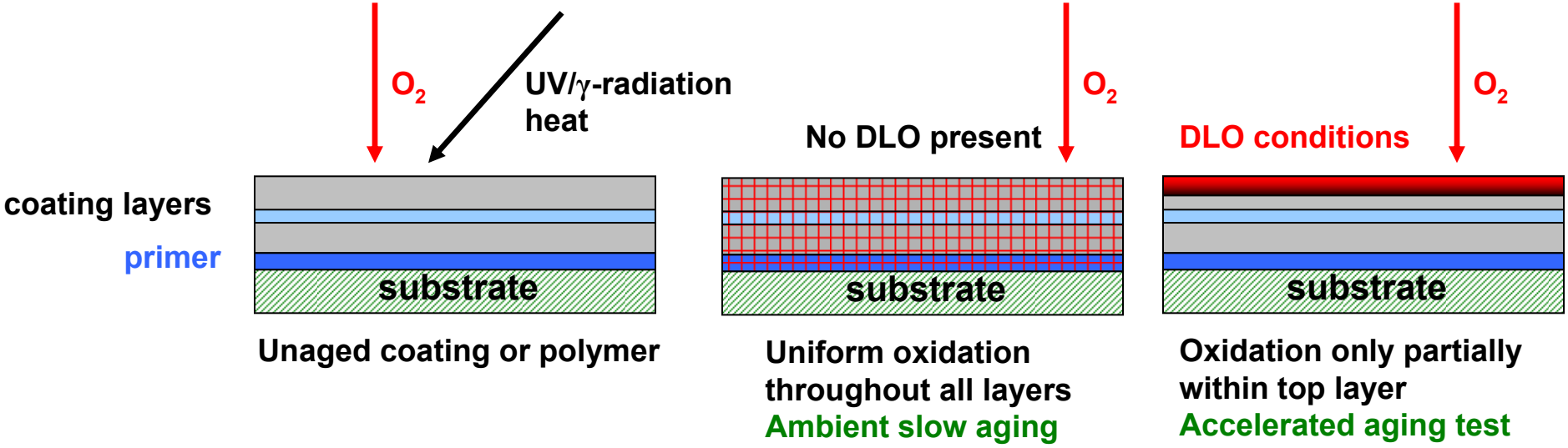
Accelerated Aging Often Involves DLO

- **DLO: Diffusion Limited Oxidation**
- **Oxidation within material is faster than oxygen can diffuse into it**
- **Leads to oxidation profile formation, heterogeneous degradation**
- **Oxidation rate *Φ* (consumption) versus permeability *P* (supply)**
- **Accelerated aging tests can completely misrepresent real aging**



Aging tests without knowing Φ and P can be convoluted by DLO
These issues are the same for thermo-oxidative or photo-oxidative
The only difference is that photo-oxidation often focuses on the top layer

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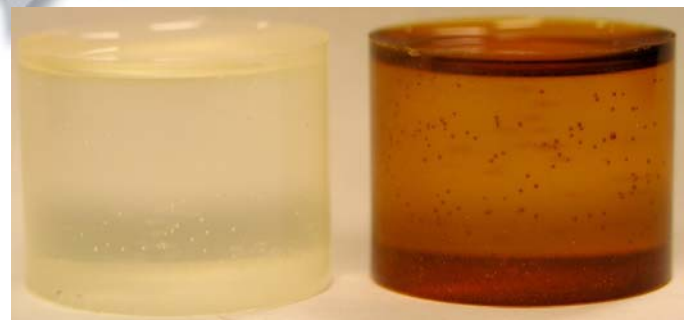
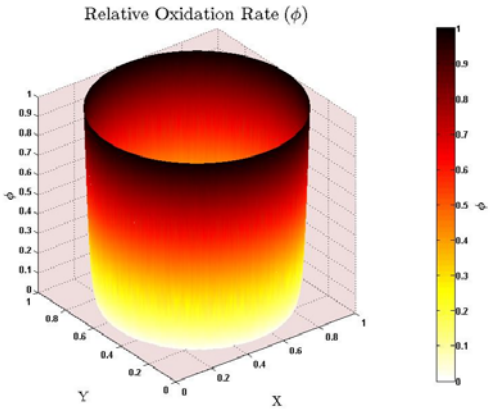
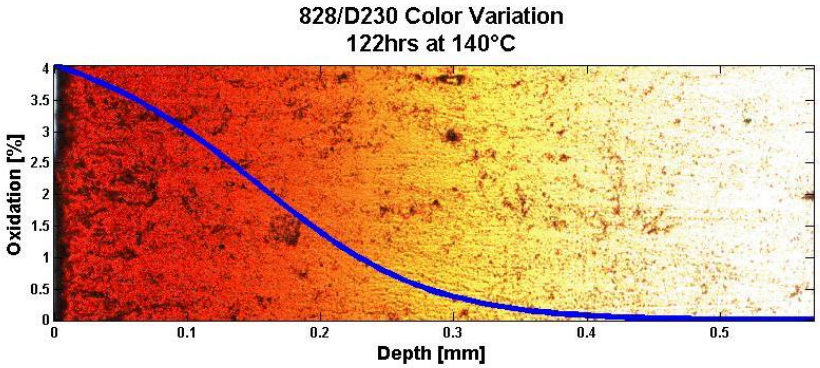
Epoxy Materials and Oxidation

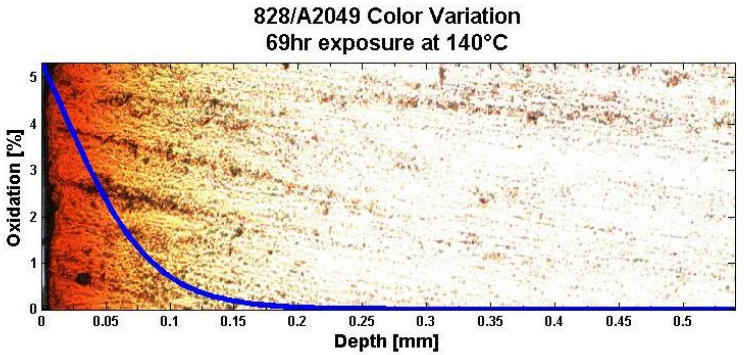


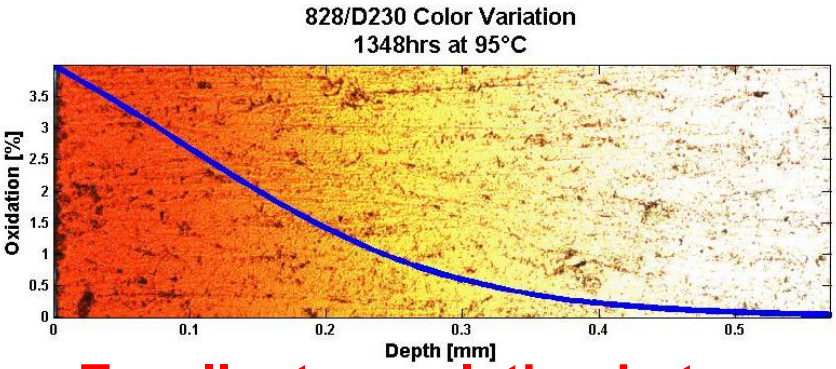
Non-aged 828/A2049 828/A2049 aged 220 days at 80°C

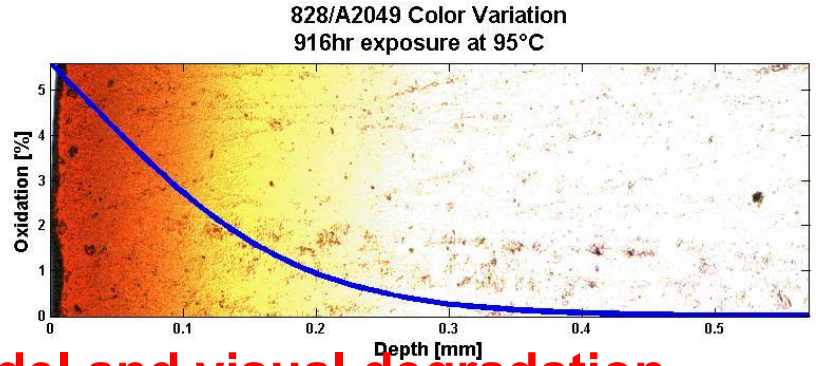
Severe degradation is limited to material surface











Excellent correlation between model and visual degradation

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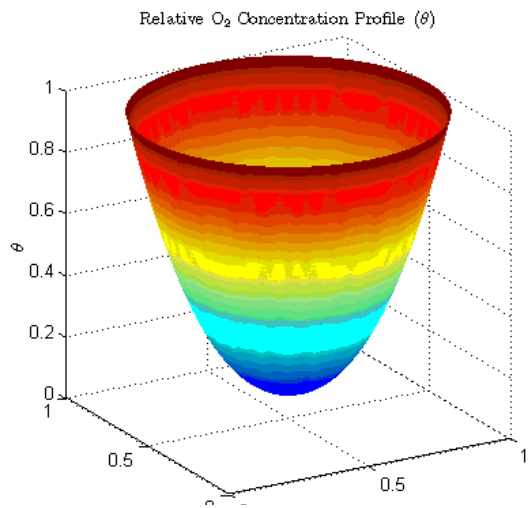
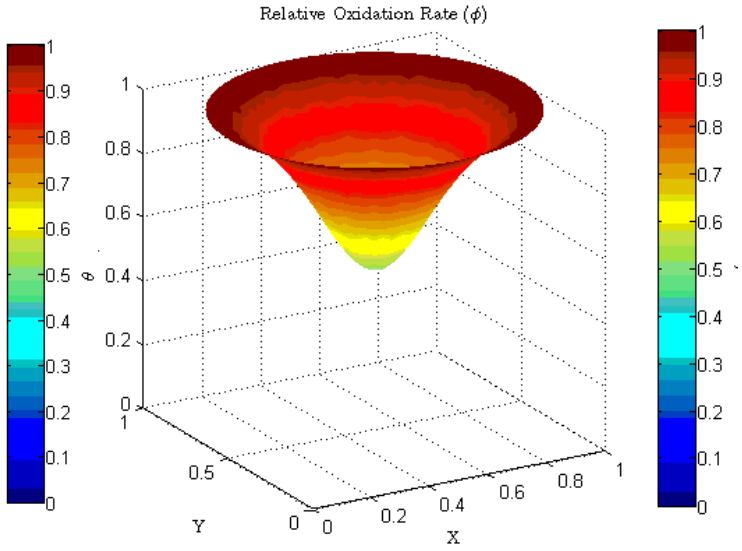
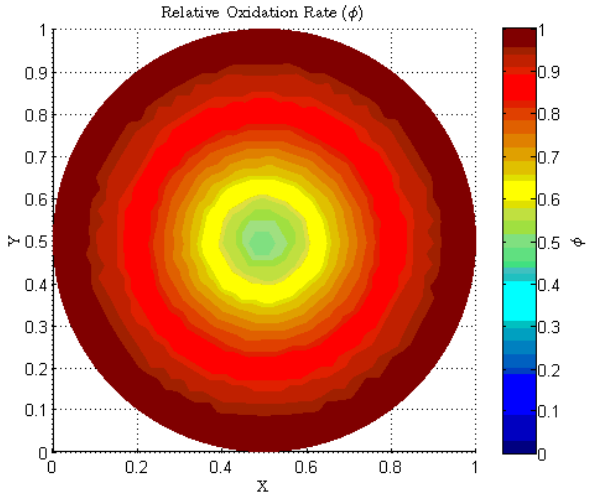
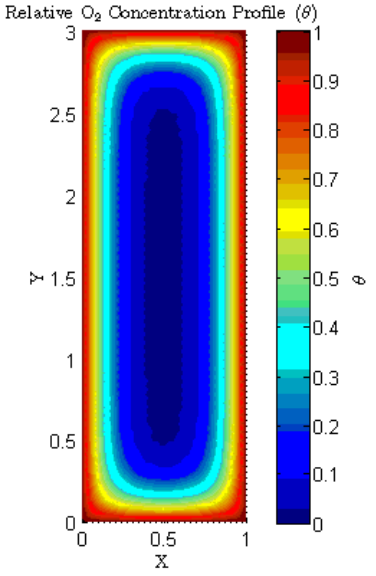
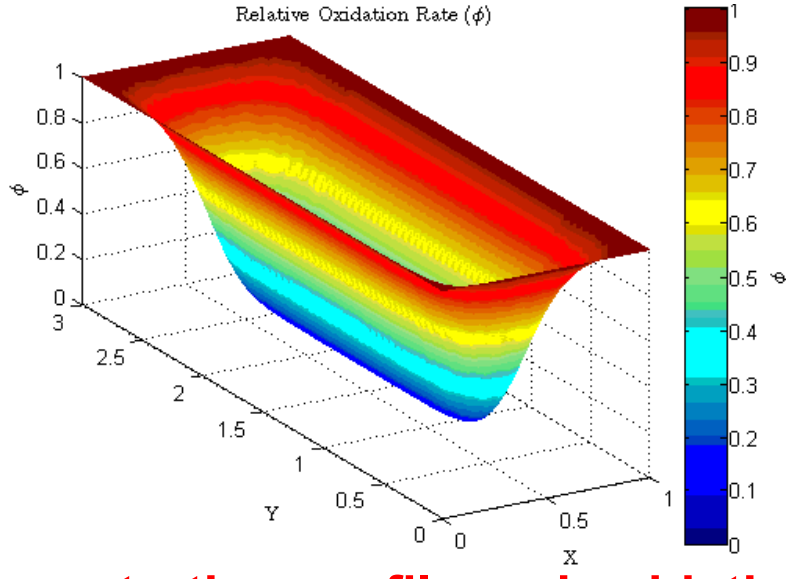
DLO 2D FE models

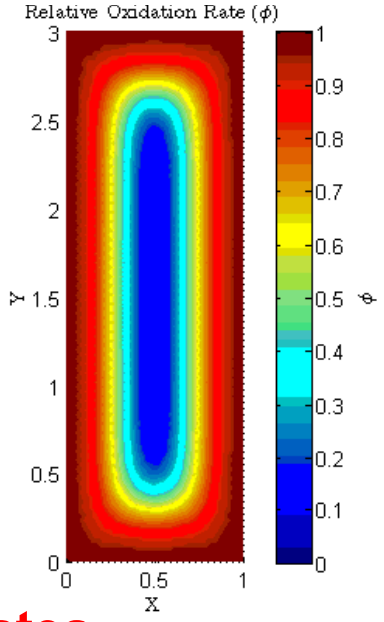












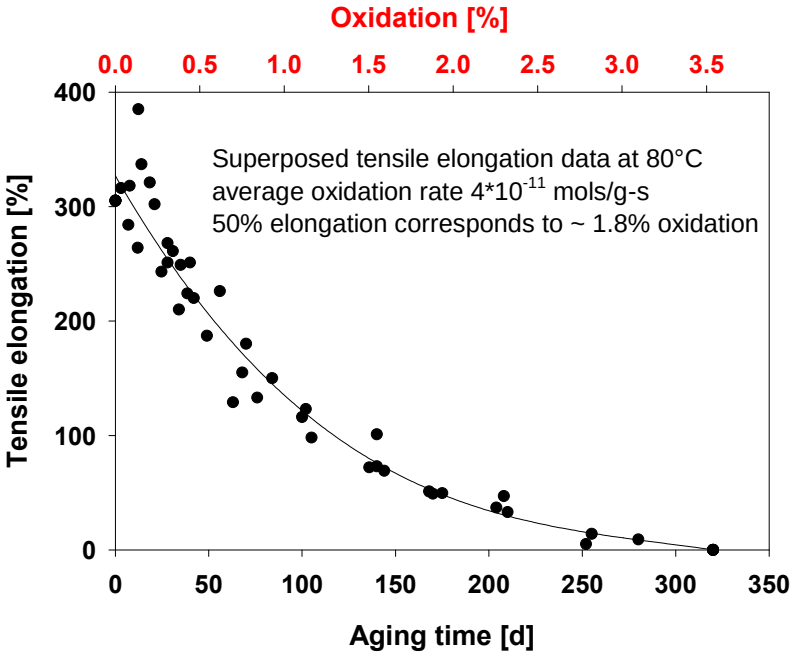
O2 concentration profile and oxidation rates

Oxidation Affects Molecular Weight

- Polymer material performance is all about changes in Mw and structure
- Mechanical properties depend on Mw and crosslink state

- In elastomers thermo-oxidation results mostly in crosslinking
- Elastomers can handle more oxidation than semi-crystalline materials
- In many polymers thermo-oxidation results in lower Mw (scission)
- Thermosets often have scission and crosslinking reactions

- **Oxidative damage impact: Semi-crystalline > Elastomers >Thermosets**



- Example HTPB (soft elastomer)
- Oxidation level affects tensile properties

- Seals harden and the material sets
- Cables lose flexibility

Celina M, Graham A, Gillen K, Assink A, Minier L, Rub Chem Tech 2000;73:680

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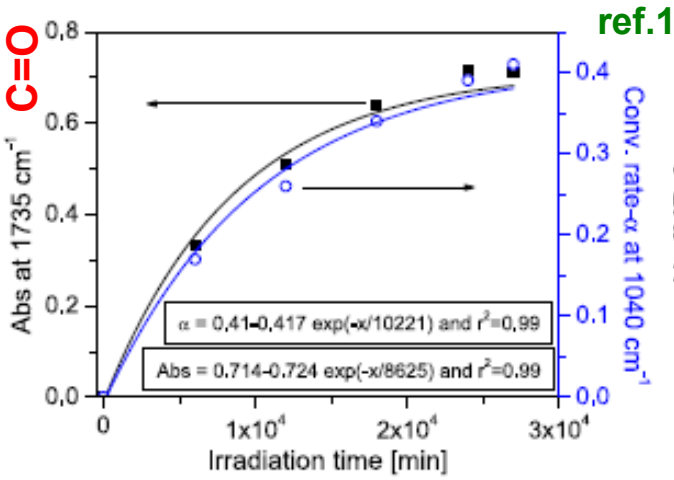
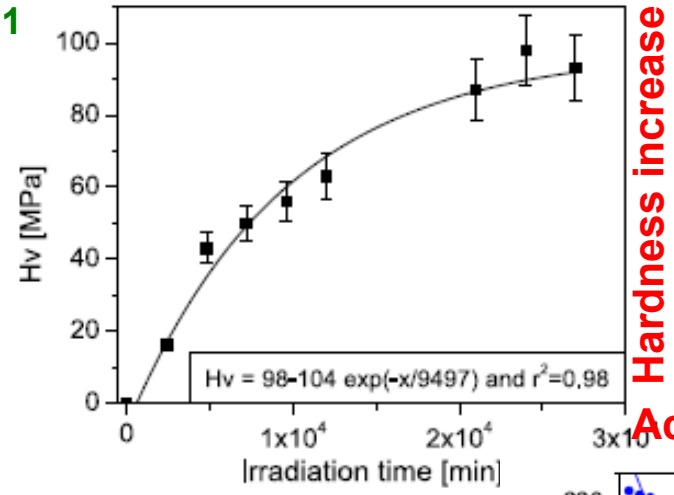
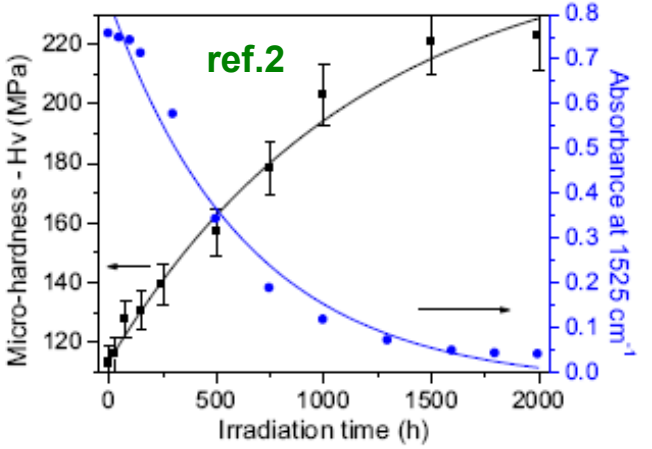
Oxidation - Mechanical Properties

- Work at Univ. Blaise Pascal, JL Gardette and colleagues
- Photo-degradation is strongly heterogeneous with depth
- Thermoset oxidation chemistry and micro-hardness





Acrylic urethane thermoset



For different thermosets:

- **Excellent correlation between oxidation and hardness**
- **Coupled with surface ablation, cracking and changes in Tg**

Larche JF, Bussiere PO, Therias S, Gardette JL. Polym Degrad Stab 2012;97:25
Larche JF, Bussiere PO, Gardette JL. Polym Degrad Stab 2011;96:1438
Gardette J-L, Rivaton A, Therias S. Photochem. Photophys. Polym Mat. 2010:569

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Oxidation - Mechanical Properties

- Correlation of Mw reduction with mechanical performance
- Nice ENSAM work (Fayolle, Colin, Verdu et al) for semi-crystalline polymers

Chain scission

Decrease in Mw

Chemicrystallization

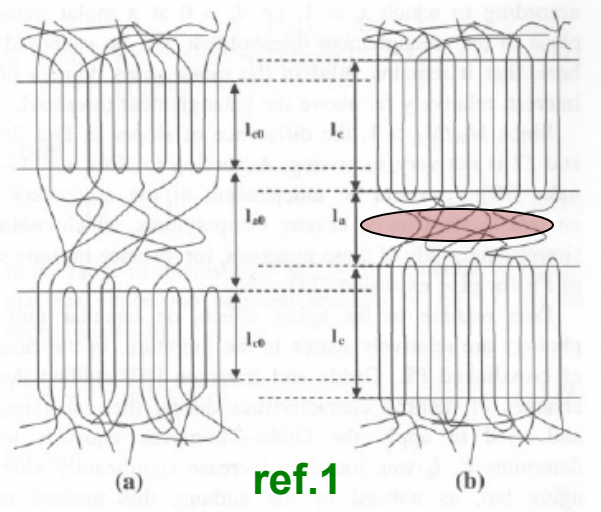
Decrease in interlamelar spacing
Decrease in tie molecules

Embrittlement

- Ductile to brittle transition
- Embrittlement at low conversion and abruptly
- Often at high overall Mw
- Toughness decrease
- Defect size increase

- Embrittlement occurs before significant entanglement network damage, at higher Mw than expected
- Damage amplification

Consequence of loss in toughness
Chain scission results in morphological changes

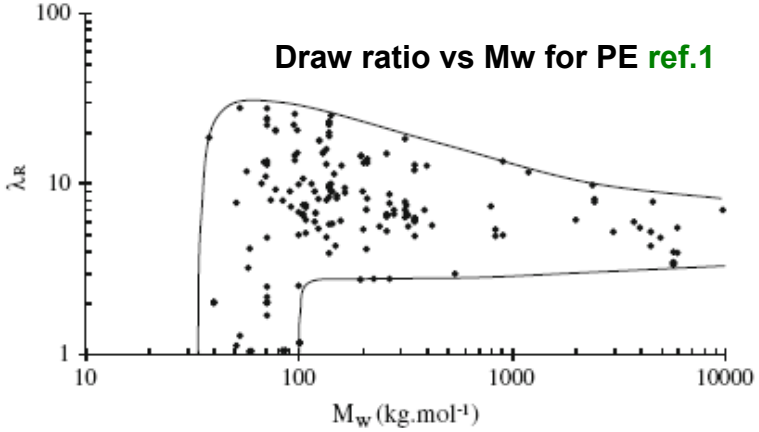


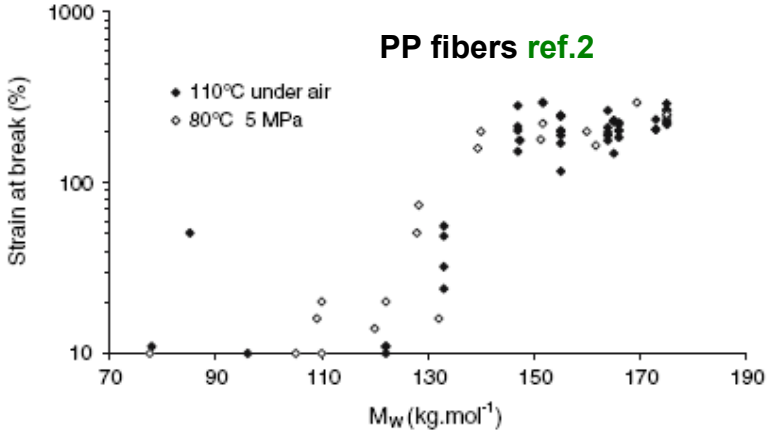
ref.1

1) Fayolle B, Richaud E, Colin X, Verdu J. J. Mat. Sci. 2008;43:6999
2) Fayolle B, Richaud E, Verdu J, Farcas F. J. Mat. Sci. 2008;43:1026
3) Fayolle B, Colin X, Audouin L, Verdu J. Polym. Degrad. Stab. 2007;92:231

Oxidation – Mw, Mechanical Properties

- ENSAM reviews (Fayolle, Colin, Verdu et al)
- Critical Mw (ductile to brittle) for a range of polymers





Polymer	Critical Mw ref.1
PC	28,000
PMMA	40,000
PS	60,000
PE	70,000
PP	200,000
PP fibers	130,000
POM	70,000
Nylon	~17,000 (X.Colin)
PTFE	~200,000 ref.3

Critical Mw data imply that very few scission events are required
Little oxidation has dramatic impact on mechanical properties

1) Fayolle B, Richaud E, Colin X, Verdu J. J. Mat. Sci. 2008;43:6999
2) Fayolle B, Richaud E, Verdu J, Farcas F. J. Mat. Sci. 2008;43:1026
3) Fayolle B et al. Polymer 2003; 44: 2773

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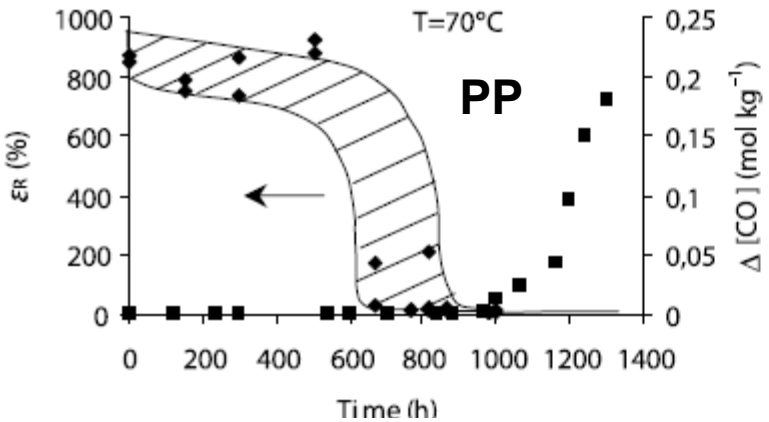
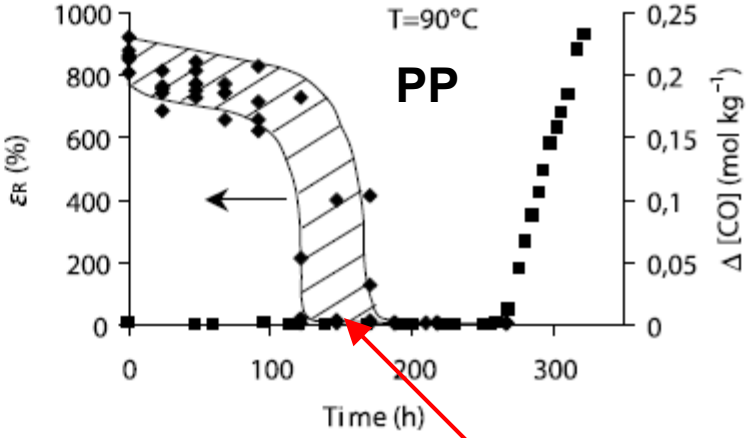
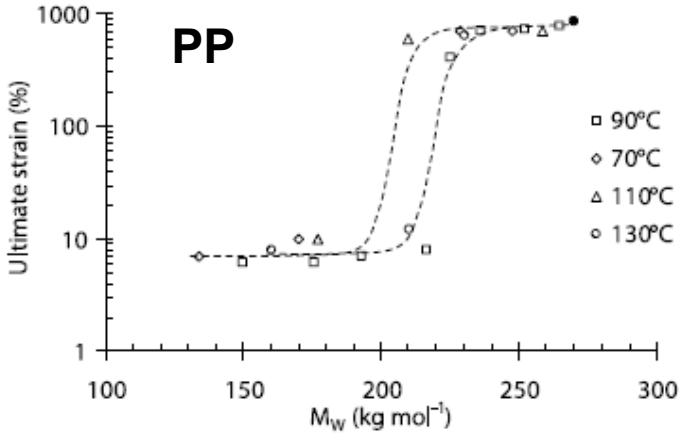
Oxidation - Mechanical Properties

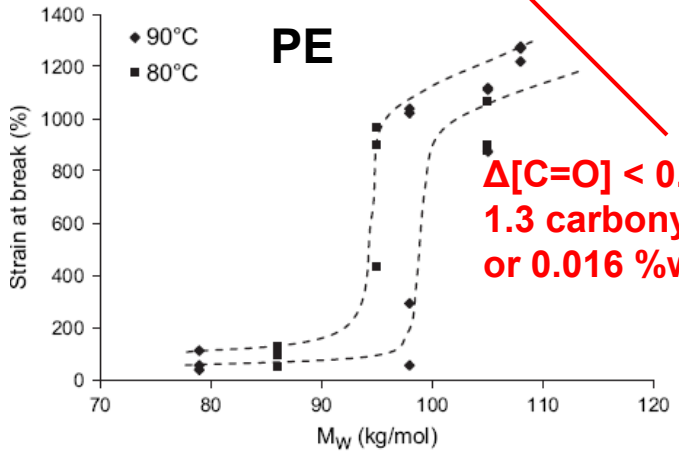
- **Mechanical property correlation with oxidation chemistry (C=O)**







From Mw = 270,000 to 180,000



From Mw = 110,000 to 85,000

Δ[C=O] < 0.005 mol/kg
1.3 carbonyl per 270,000 Mw
or 0.016 %weight oxidation

1) Fayolle B, Audouin L, Verdu J. Polymer 2004;45:4323
2) Fayolle B, Colin X, Audouin L, Verdu J. Polym. Degrad. Stab. 2007;92:231

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Oxidation Level and Mw Changes

- Oxidative scission results in Mw reductions
- Scission yield (efficiency) is not always known
- But pre-oxidation levels (hydroperoxides) and oxidation is often modeled

Assume PP chain scission from Mw = 400,000, even splits, cleavage points from hydroperoxide decay with beta-scission

Scissions in PP	Mw	Oxidation [%]	Oxidation [mol/l]
0	400,000	-	-
1	200000	0.008	0.00225
3	100000	0.024	0.0067
9	40,000	0.072	0.0675

PP critical oxidation ~0.01 – 0.02%

Initial [ROOH] in ENSAM kinetic models
~ 10-4 mol/l or ~10% of critical oxidation

Nylon with Mw = 50,000 degrading to 20,000
Effective scission via C--N cleavage
~ 0.2% oxidation (0.072 mol/l)

- **Coupling Mw data with precise oxidation will deliver effective scission yields**
- **High efficiency scission reactions allow for estimation of critical oxidation**
- **Mechanistic studies are often conducted beyond the critical oxidation level**

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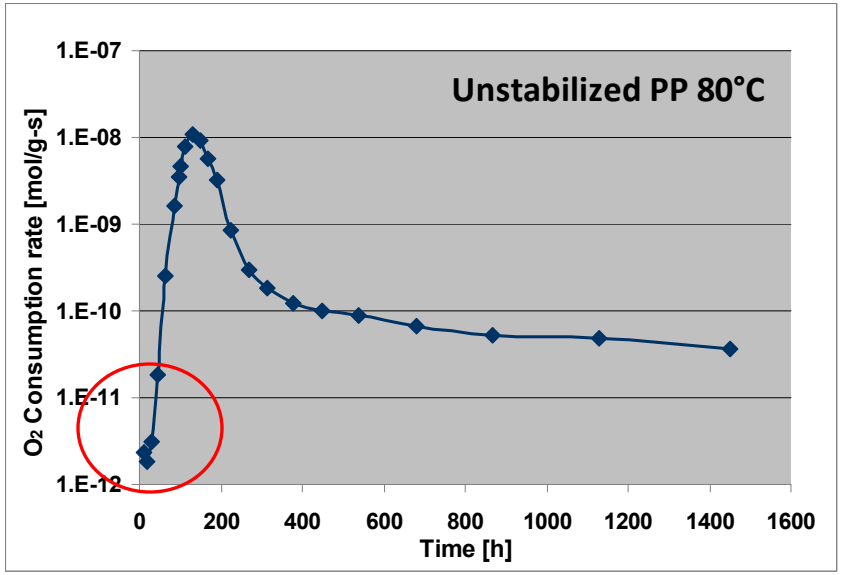
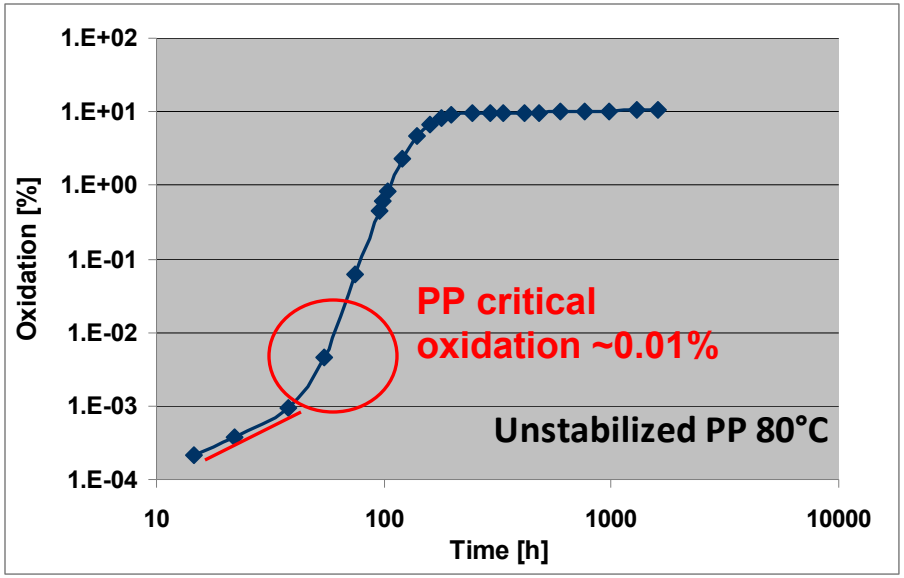
Probing of min. Oxidation Level in PP

- Used Oxzilla to probe oxuptake vs time for PP auto-oxidation at 80°C
- Proof of concept for unstabilized material



4 orders of magnitude rate acceleration



PP tind. oxidation ~0.001%

- From CL studies in the 90's we know that embrittlement is soon after tind.
- 0.01% oxidation is nicely within the early auto-oxidation phase
- Consistent with sufficient chain scission for reduction in critical Mw

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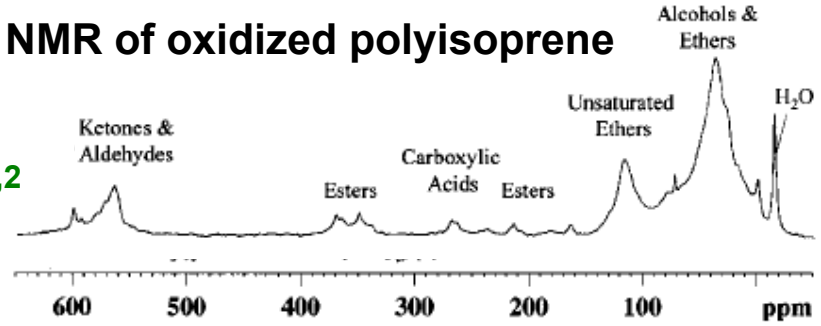
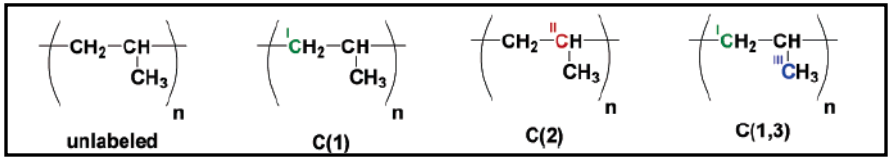
Mechanistic Studies – Isotopic Labeling

- Use isotopic reagent ($^{17}O_2$, NMR, $^{18}O_2$ IR) or markers in polymer (^{13}C)
- Demo work in 1997 (oxidative degradation of elastomers)
- Selective signature of generated species or degradation derivatives

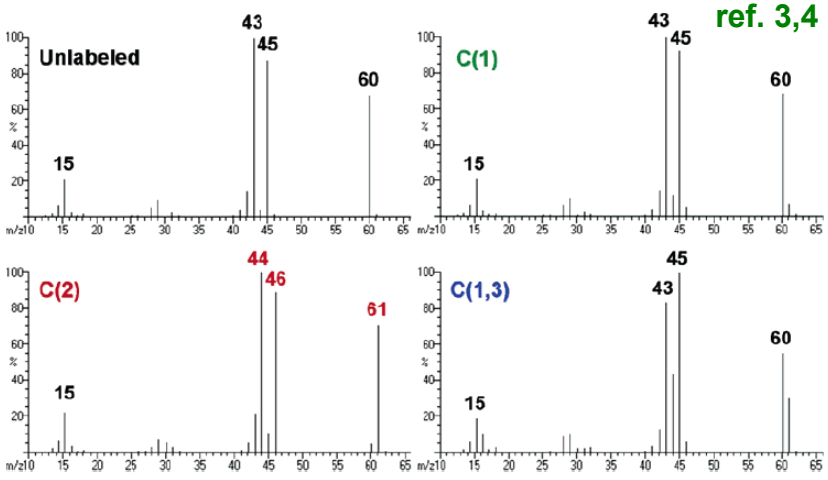
^{17}O NMR of oxidized polyisoprene

ref.1,2





ref. 3,4



- Oxidation chemistry in the polymer
- Volatile species identification (GC-MS)
- Complex degradation mechanisms
- Thermal and radiation processes

Continued in-depth work for PP and Nylon (Bernstein, Clough)
Pathways for volatile generation and identification of attack sites

1) Alam TM, Celina M, Wheeler DR, Assink RA, Clough RL, Gillen KT. Polymer News 1999;24:186
2) Alam TM, Celina M, Assink RA, Clough RL, Gillen KT, Wheeler DR. Macromolecules 2000;33:1181
3) Thornberg SM et al. Insights into Oxid. Pathways, from Gas. Products of PP… Macromolecules 2006;39:5592
4) Thornberg SM et al. The genesis of CO2 and CO in the thermooxid. degrad. of PP. *Polym Degrad Stab* 2007;92:94

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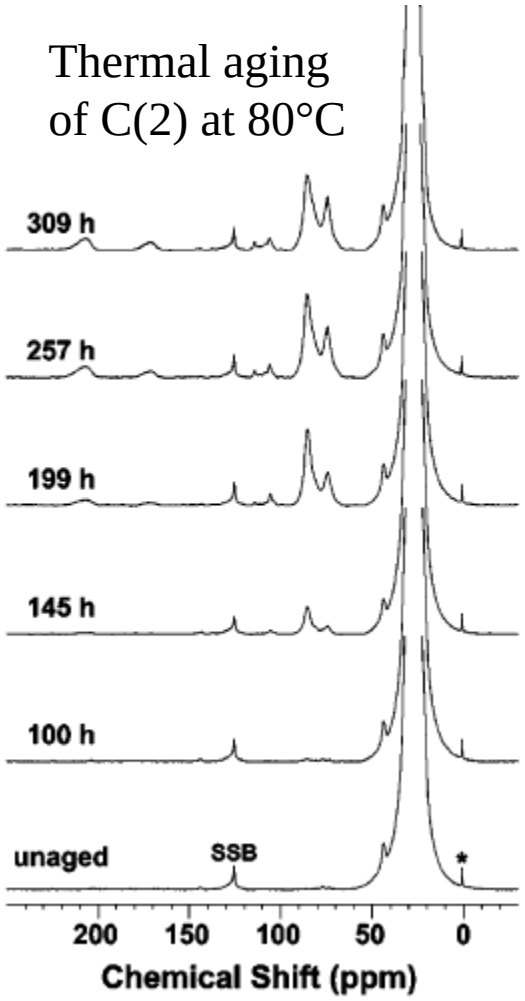
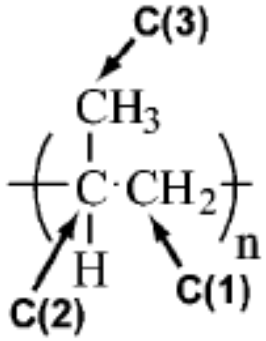
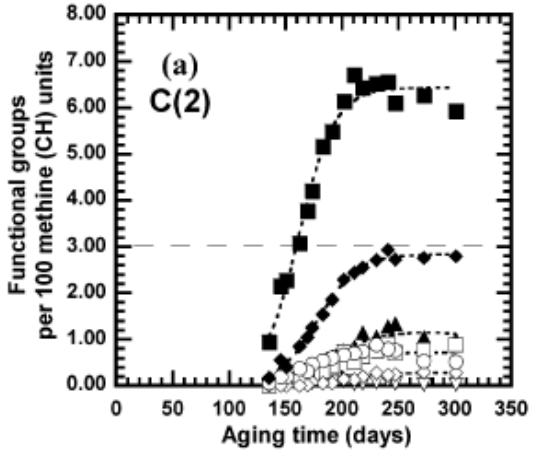
^{13}C Labeled PP Model Degradation





- **Thermal, radiation degradation**
- **Highly sensitive**
- **Chemical species**
- **Reaction kinetics**



ROOH >ROH>RCOR

^{13}C chemical shift (ppm)	Functional group		PP position of origin	Aging conditions observed[a]
~215 (broad)	~CH(CH3)C(=O)CH~	in-chain ketone	C(1)	Δ (50 °C, 80 °C, 109 °C) γ (80 °C)
~207 (broad)	~CH(CH3)CH2C(=O)CH3	methyl (chain-end) ketone	C(2)	Δ (50 °C, 80 °C, 109 °C) γ (24 °C, 80 °C)
~185 (broad)	~CH(CH3)CH2C(=O)OH	carboxylic acid	C(2)	Δ (50 °C) γ (24 °C)
~179 (broad)	~CH(CH3)C(=O)OH	carboxylic acid	C(1)	Δ (50 °C, 80 °C, 109 °C) γ (24 °C, 80 °C)
	~CH(CH3)C(=O)OR	ester		
170–175 (broad)	~CH(CH3)CH2C(=O)OR	ester	C(2)	Δ (50 °C, 80 °C, 109 °C) γ (24 °C, 80 °C)
	~CH(CH3)CH2C(=O)OOR	perester		
100–117 (several peaks)	~O-C(-O~)-O~	ketal	C(1) C(2)	Δ (50 °C, 80 °C, 109 °C) γ (24 °C, 80 °C)
	~O-CH(~)-O~	acetal		
85.3	~CH2C(CH3)(OOH)CH2~	tertiary hydroperoxide	C(2)	Δ (50 °C, 80 °C, 109 °C) γ (24 °C, 80 °C)
	H3C-COOC-CH3	dialkyl peroxide		
74.2	~CH2C(CH3)(OH)CH2~	tertiary alcohol	C(2)	Δ (50 °C, 80 °C, 109 °C) γ (24 °C, 80 °C)

Mowery D, Assink R, Derzon D, Klamo S, Clough R, Bernstein R, Macromolecules, 2005;38:5035

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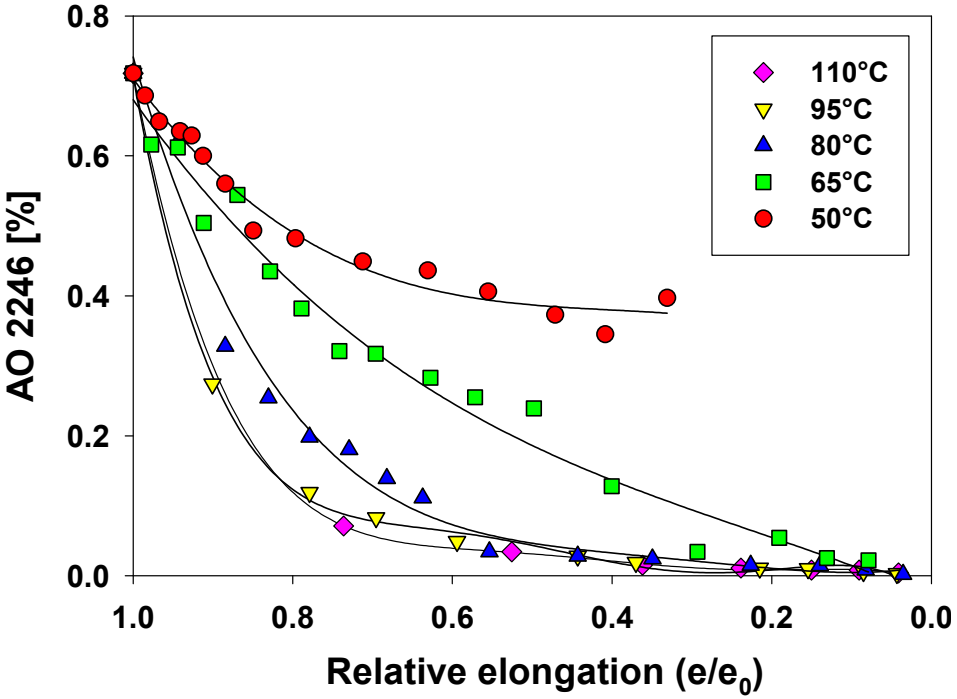
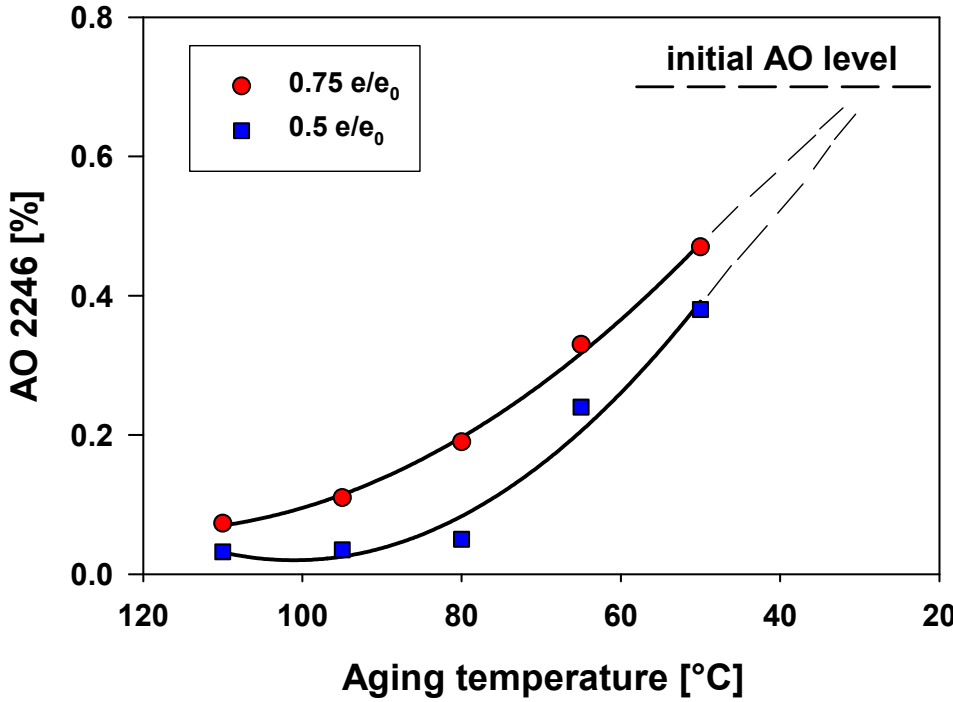
Antioxidant Loss - Degradation in HTPB

- Rapid decrease in AO at elevated T
- Continued presence of AO at lower T

AO depletion depends on T



Loss of mech. properties at diff. AO levels



- No universal correlation between AO level and mechanical properties
- Aging and failure will occur at low T's despite high levels of active AO

M. Celina, J. Skutnik Elliott, S. Winters, R. Assink, and L. Minier, *Poly. Deg. Stab., 91* (2006) 1870

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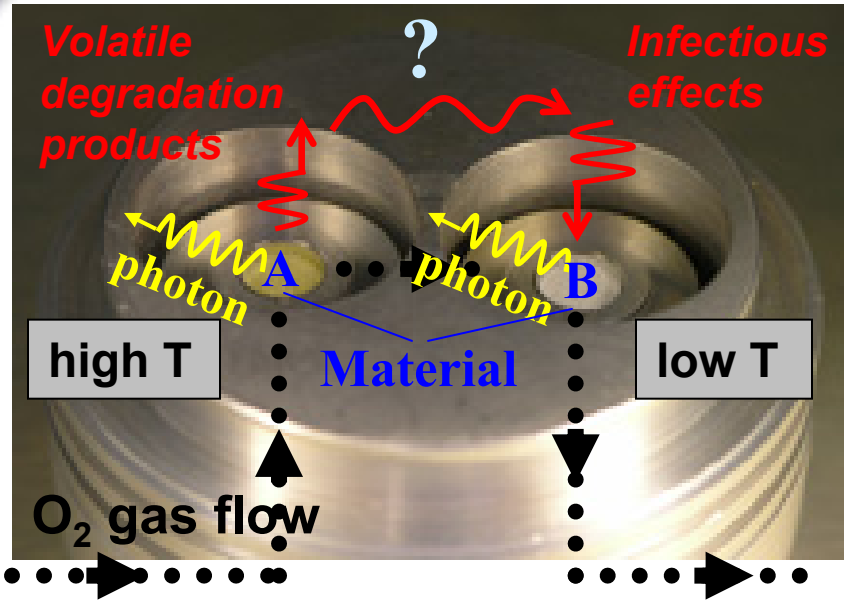
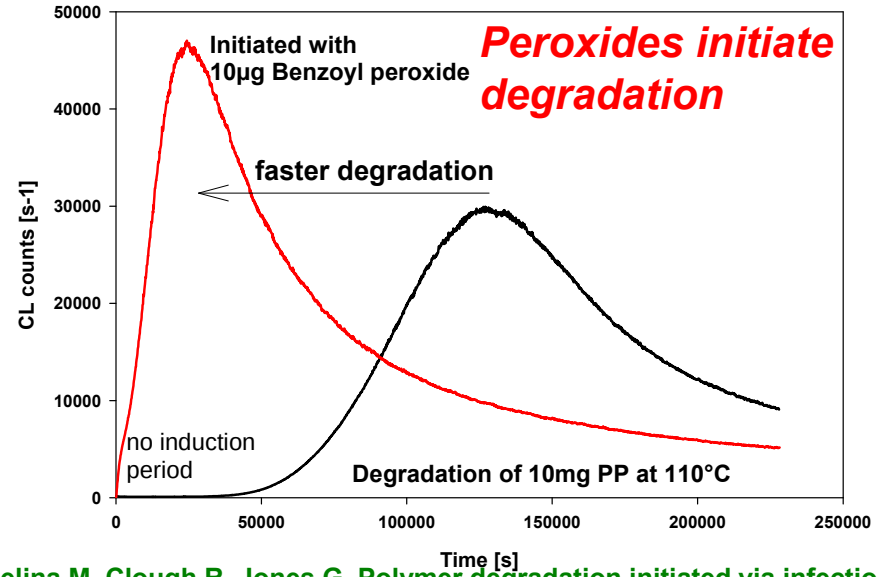
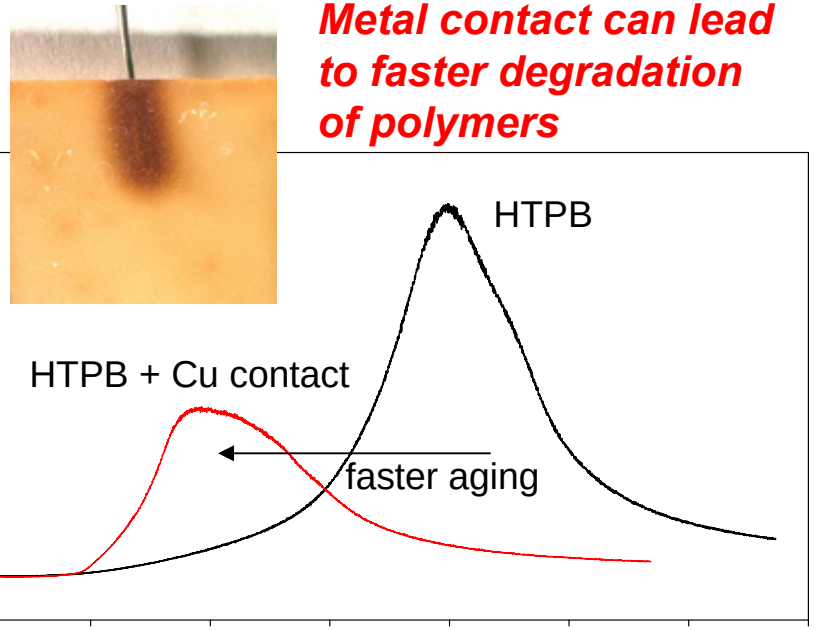
Contaminants Affect Degradation

CL monitoring of degradation processes



- Volatile species will be produced during degradation of polymer
- They initiate degradation of less reactive material
- Volatile antioxidants can retard degradation
- Detrimental effects of metal ions



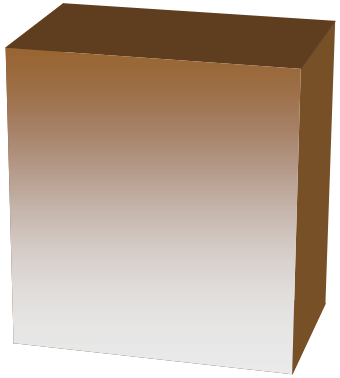


Celina M, Clough R, Jones G. Polymer degradation initiated via infectious behavior. Polymer 2005;46:5161

Examples of Infectious Processes

Ethylene gas ripens fruit

Unripe avocado + ripening apple



Ripening fruit releases ethylene, which causes OTHER fruit to ripen

$CH_2=CH_2$

ripe avocado

Tin disease causes infected metal to contaminate other metal

buttons degraded

Napoleon's army left Russia with their pants down

Summary

- Thermo-oxidative degradation of polymers is unavoidable
- Understanding polymer behavior and lifetime prediction involves many aspects of the material and degradation processes
- Thermo-oxidative degradation depends on how O_2 can interact with the polymer
- Physics and chemistry combine in diffusion limited oxidation (DLO)
- Accelerated thermo-oxidation, photo-aging, radiation aging, OIT-DSC, TGA all depend on DLO
- We can accurately measure oxidation rates and use them for lifetime prediction

- Thanks for your attention and hopefully there was something of interest!

QUESTIONS?

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