Ozone and Fatigue Resistance of NR/EPDM blends in Tire Sidewall Applications

William V. Mars*, Erick Sharp, Jaden Slovensky, Yang Chen, Ethan Steiner

Tire Society 2022

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Ozone Resistance Just Got Harder

TABLE II

GENERAL RESISTANCE OF ELASTOMERS TO OXIDATIVE DEGRADATION

A. Elastomers Resistant to Oxidation

Elastomer	ASTM Designation
Acrylic	ACM
Chloro-sulfonyl-polyethylene	CSM
Ethylene propylene diene	EPDM
Fluoroelastomers	FKM
Ethylene oxide epichlorohydrin	ECO
Silicones	MQ, VMQ, FVMQ
Polyester urethanes	AU
Polyether urethanes	EU
Butyl rubber	IIR
Halobutyl rubber	BIIR, CIIR

saturated

B. Elastomers not Resistant to Oxidation

Elastomer	ASTM Designation
Natural rubber	NR
Isoprene rubber	IR
Styrene-butadiene rubber	SBR
Poly(butadiene)	BR
Nitrile rubber	NBR
Neoprene	CR

unsaturated

Robert W. Keller (*1985*) Rubber Chemistry and Technology: July 1985, Vol. 58, No. 3, pp. 637-652.

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May 24, 2022 03:31 PM

USTMA backs California's plan to study 6ppd, coho salmon

Rubber News Staff

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U.S. TIRE MANUFACTURERS ASSOCIATION

Tire Industry Project.

WASHINGTON—The tire manufacturing additive 6ppd, an antioxidant and antiozonant essential to passenger safety and harmful to coho salmon when transformed into 6pp-quinone, has been elevated in priority as a substance to be studied.

This was due, in part, to the efforts of the U.S. Tire Manufacturers Association, which on May 23 endorsed a same-day decision by the California Department of Toxic Substances Control to list 6ppd as a "priority product" under the Safer

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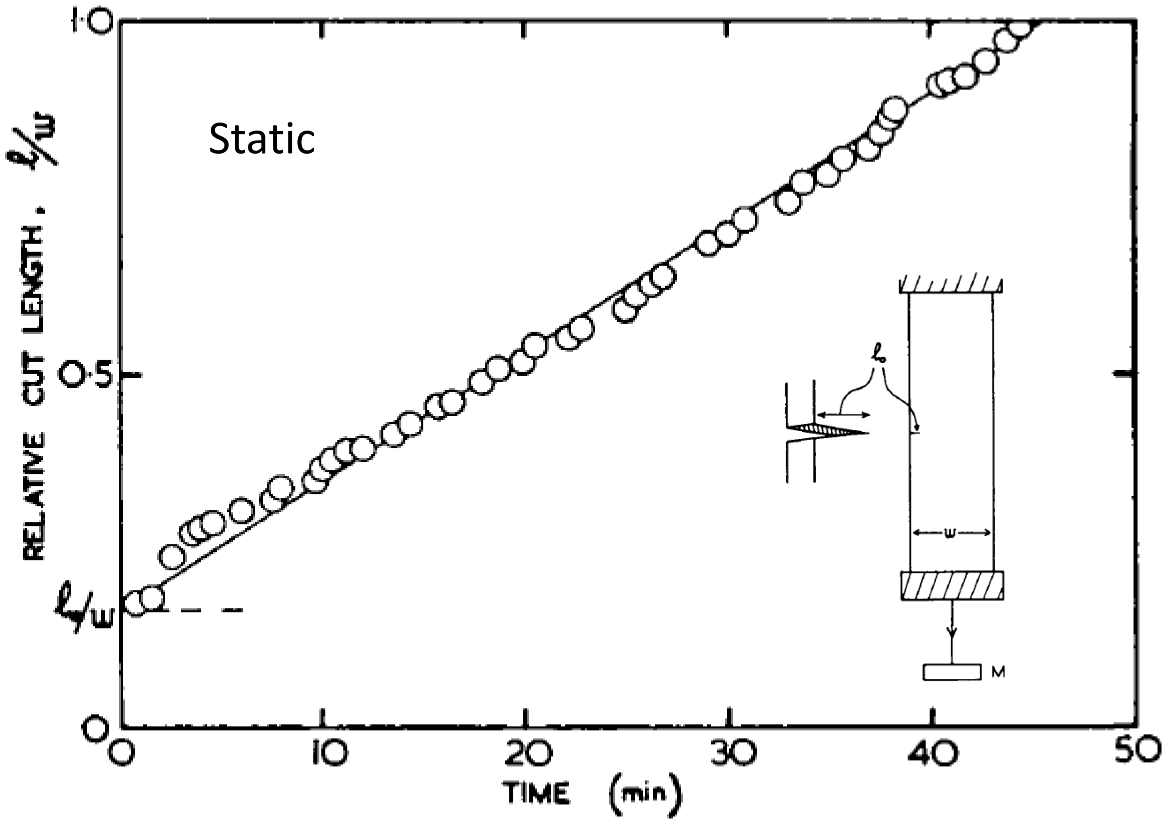
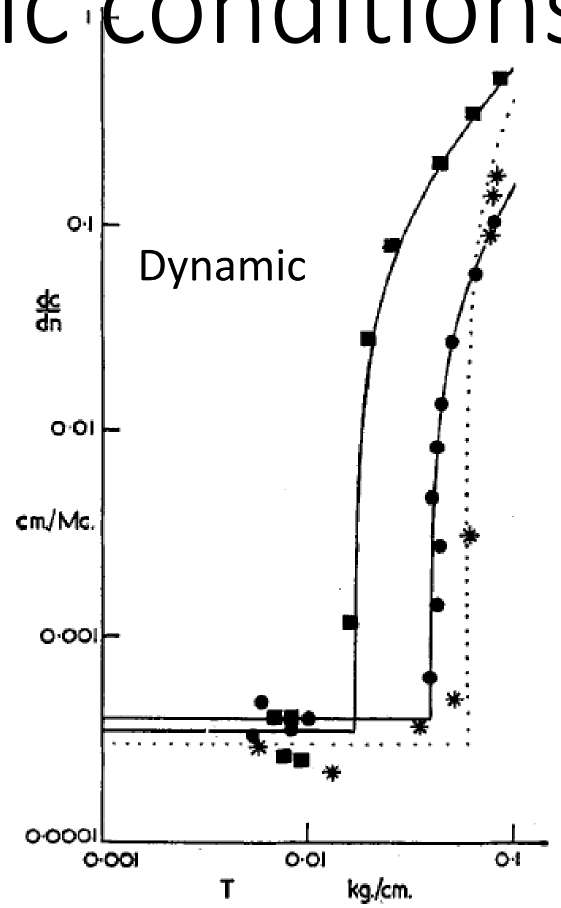
Ozone Attack: static vs dynamic conditions



M. Braden and A. N. Gent (1962) Rubber Chemistry and Technology: Vol. 35, pp. 200-209.



G. J. Lake and P. B. Lindley, Rubber Chemistry and Technology Sep 1966, Vol. 39, No. 4 (September 1966) pp. 1053-1064

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Williams Ozone Attack Model

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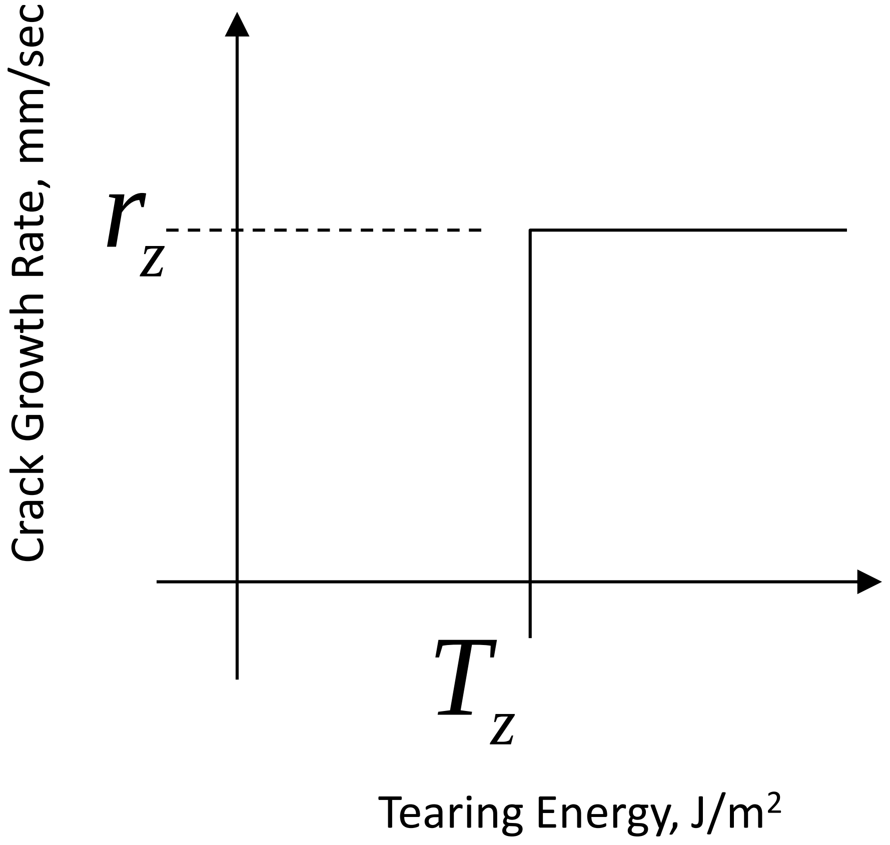
Fatigue Analysis Software




```
**MATERIAL

MAT=RUBBER
…
OZONEATTACK_TYPE=WILLIAMS  ← ozone attack model
TZ=0.1 ! J/m^2 (unprotected rubber)
RZ=0.12E-14 ! m/sec
```

Williams Ind Eng Chem 18 4 369 1926

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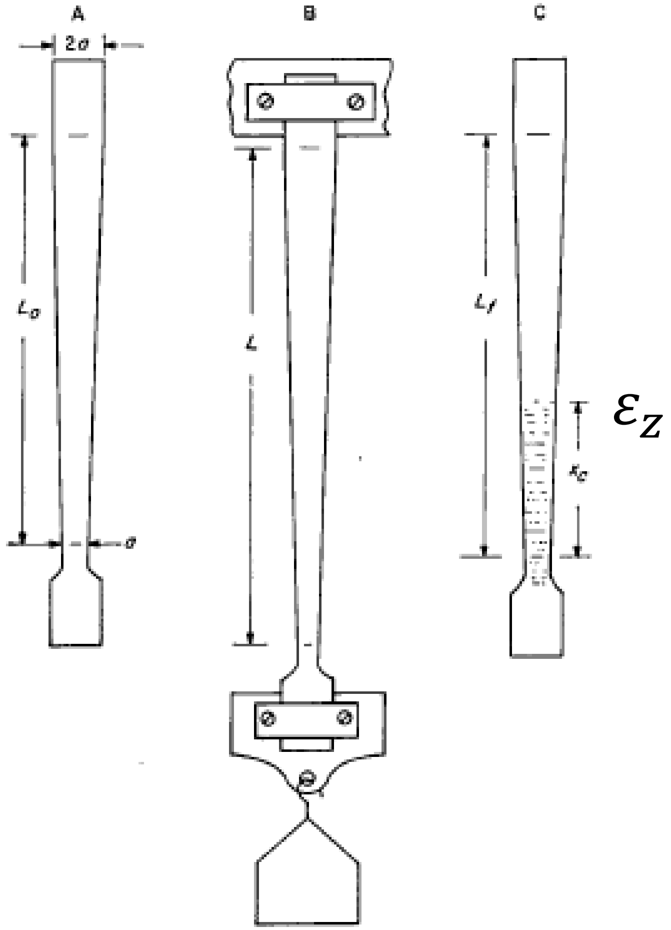
Ozone-Critical Strain -> Tz

$$T_z = 2kW_z a \qquad k \approx \pi$$

$$W_z = \frac{T_z}{2ka} = \frac{1}{2}\frac{\sigma_z^2}{E} = \frac{1}{2}E\varepsilon_z^2$$

$$T_z = kE\varepsilon_z^2 a$$

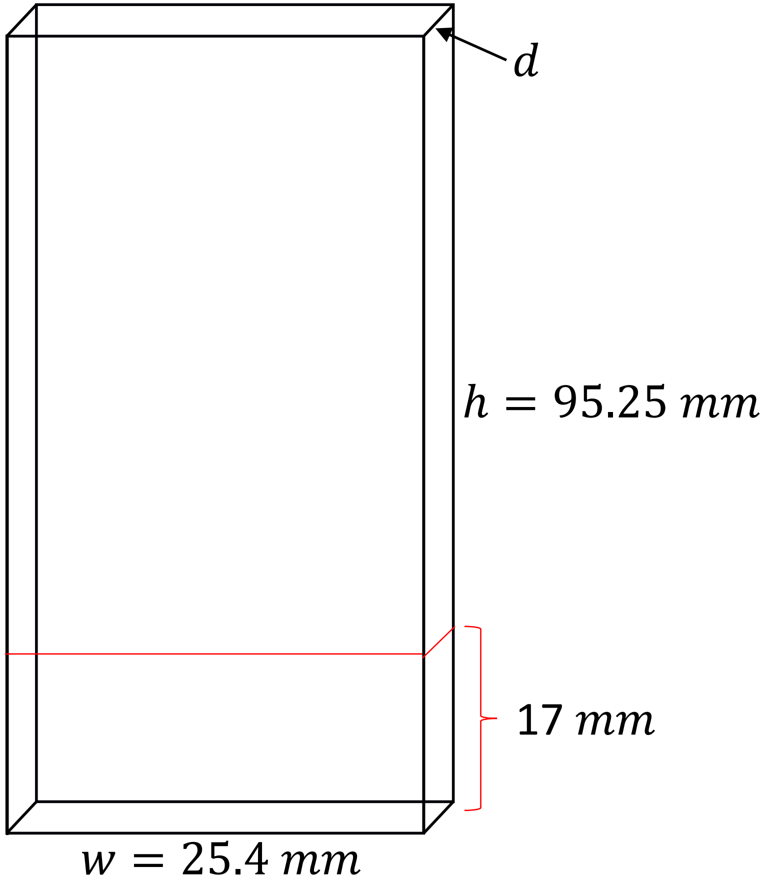


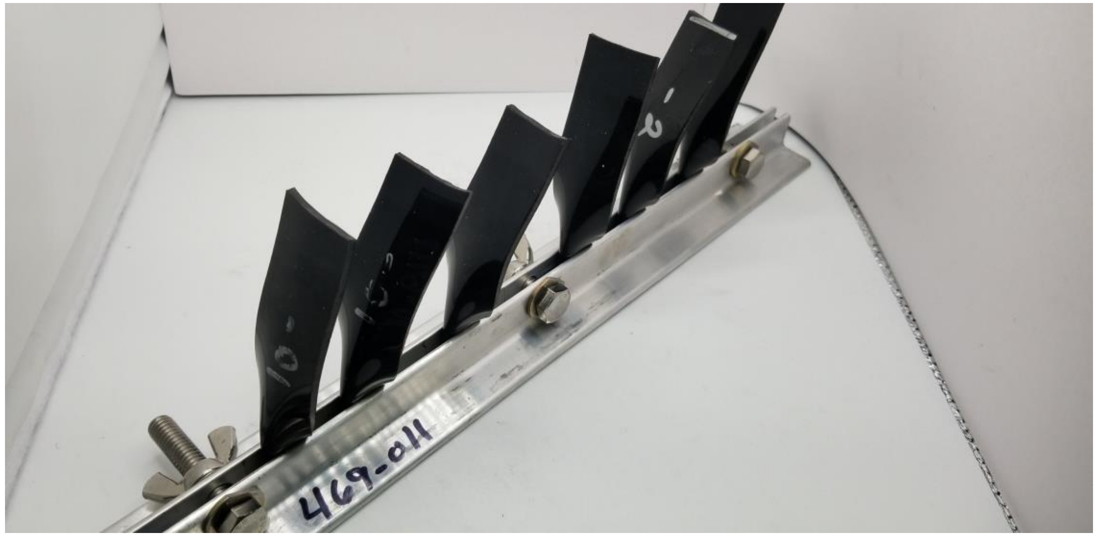
Z. W. Wilchinsky and E. N. Kresge (1974) A Quantitative Test for Ozone Resistance of Rubber Vulcanizates. Rubber Chemistry and Technology: September 1974, Vol. 47, No. 4, pp. 895-905.

Materials: NR/EPDM Blends

FORMULARY		ACE Target Requirement	Variant 1	Variant 2	Variant 3	Variant 4
First Pass						
NR	CV60		100.00	80.00	70.00	50.00
EPDM	Royalene 301T		-	20.00	30.00	50.00
	N330		45.00	45.00	45.00	45.00
	790 Oil		8.00	8.00	8.00	8.00
	Zinc Oxide		5.00	5.00	5.00	5.00
	Stearic Acid		2.00	2.00	2.00	2.00
	Sulfur		0.80	0.80	0.80	0.80
	Vultac 710		1.00	1.00	1.00	1.00
	TBBS		1.00	1.00	1.00	1.00
	ZBDC		1.00	1.00	1.00	1.00

Experiment setup



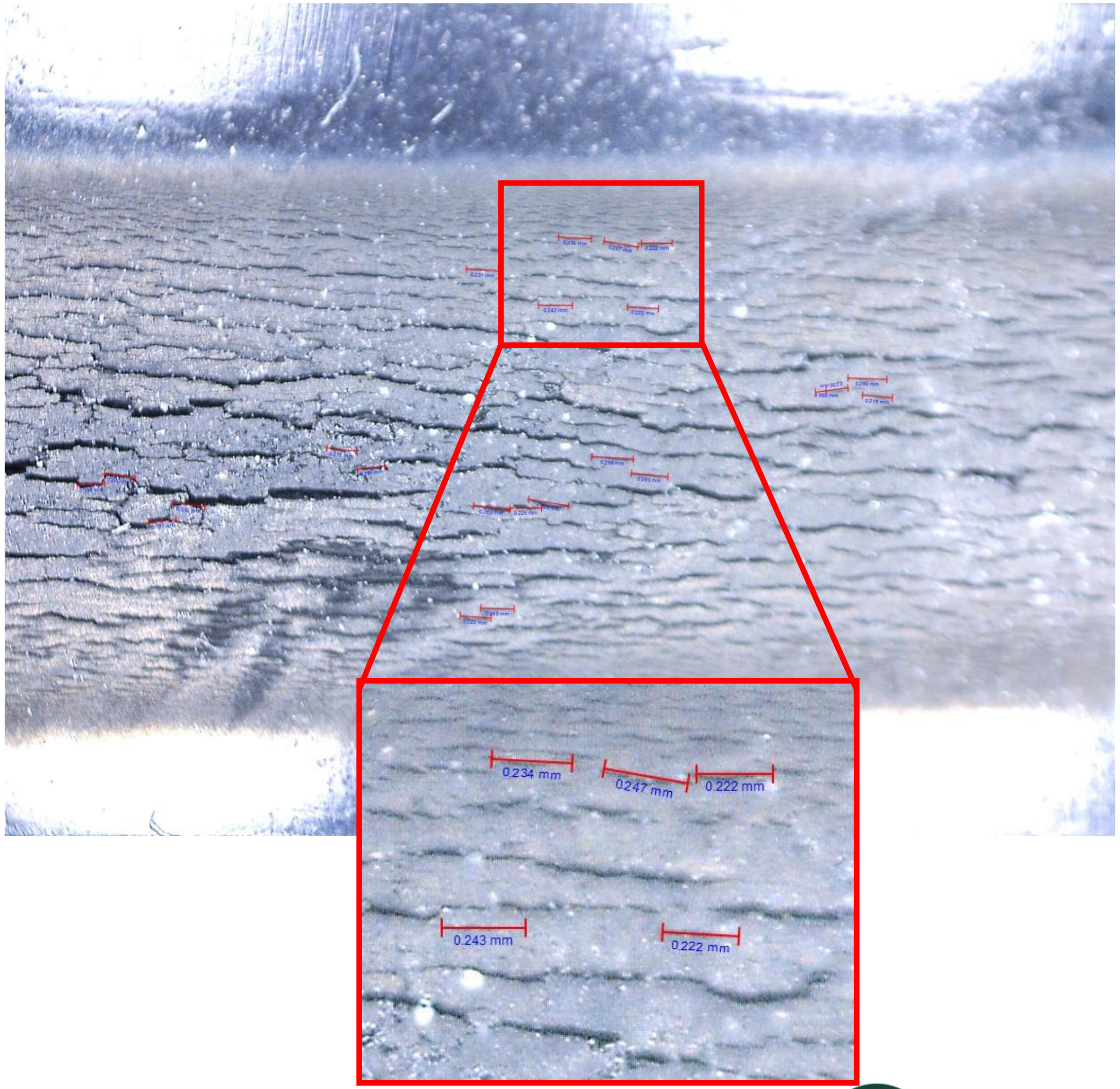


- Strain gradient is produced by bending.
- Clamped end: high curvature produces large bending strain.
- Free end: low curvature produces small bending strain

Determining r_z

- Exposure Time = 168 Hours
  - 6.05E+5 seconds
- Ozone Concentration
  - 100 parts Ozone per hundred million air particles
- $r_z = \dfrac{length\ of\ crack}{period\ of\ test}\ mm/s$

r_z	1	2	3	4
mm/s	3.54E-07	2.99E-07	1.32E-07	0



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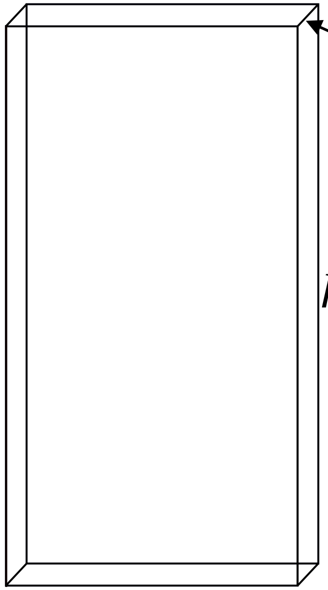
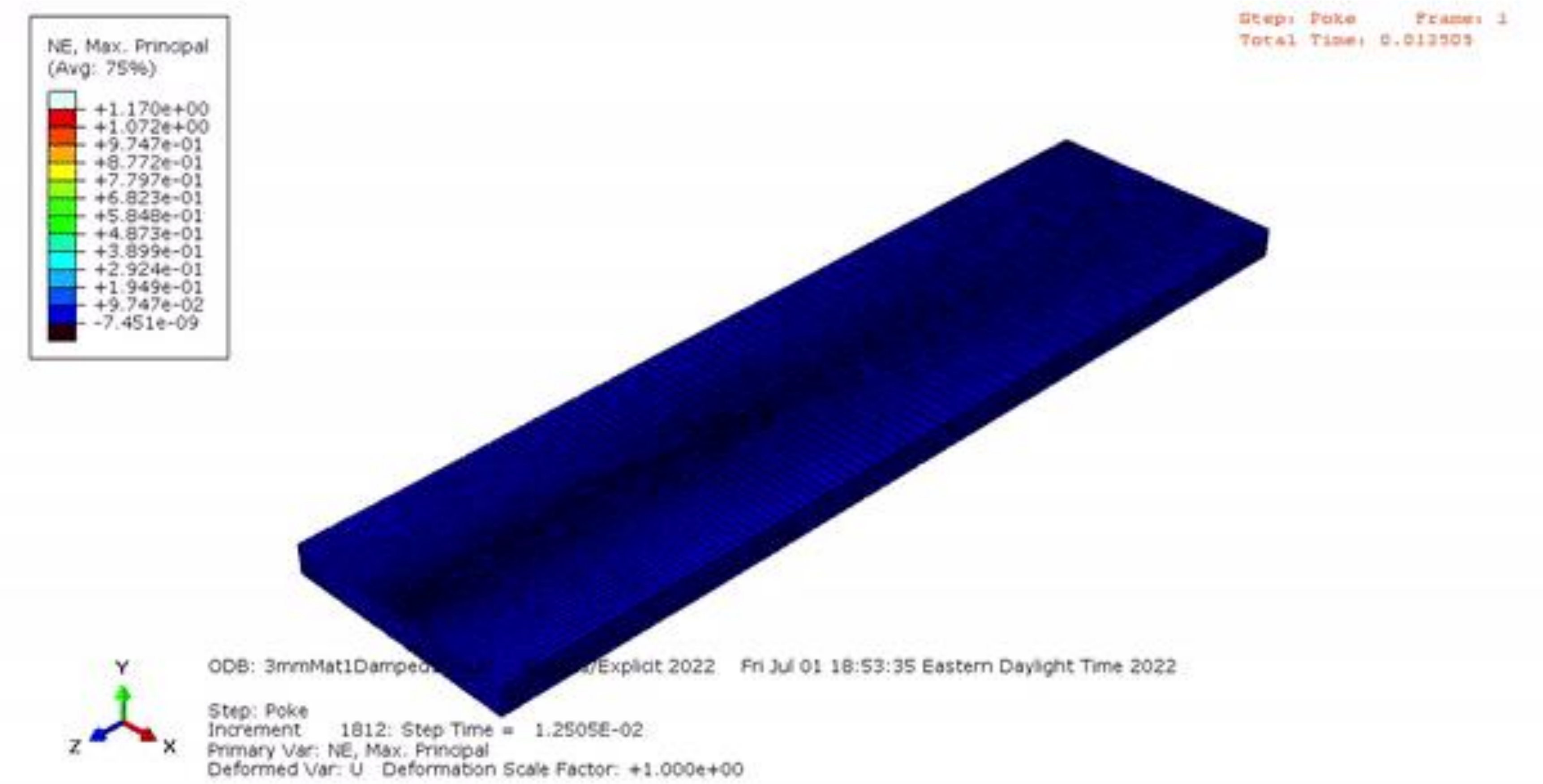
Determining ε_z and T_z





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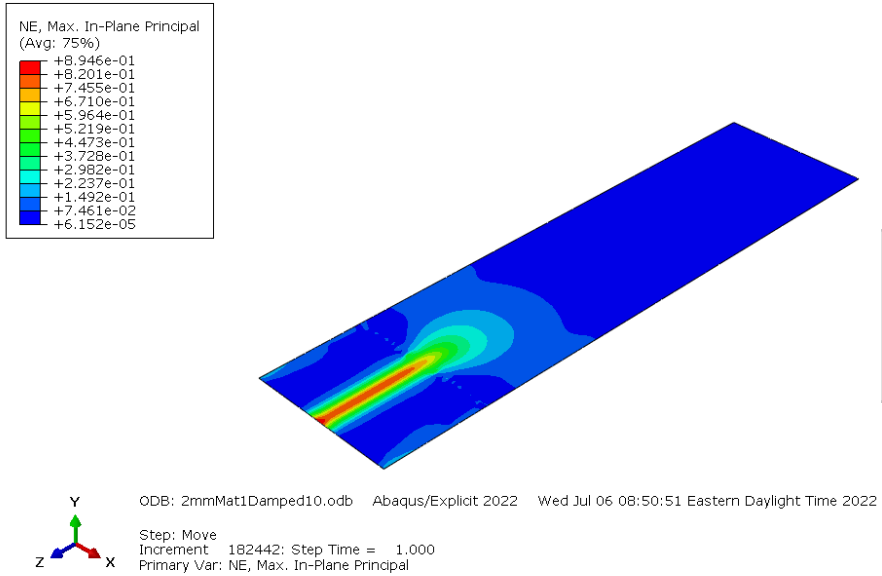
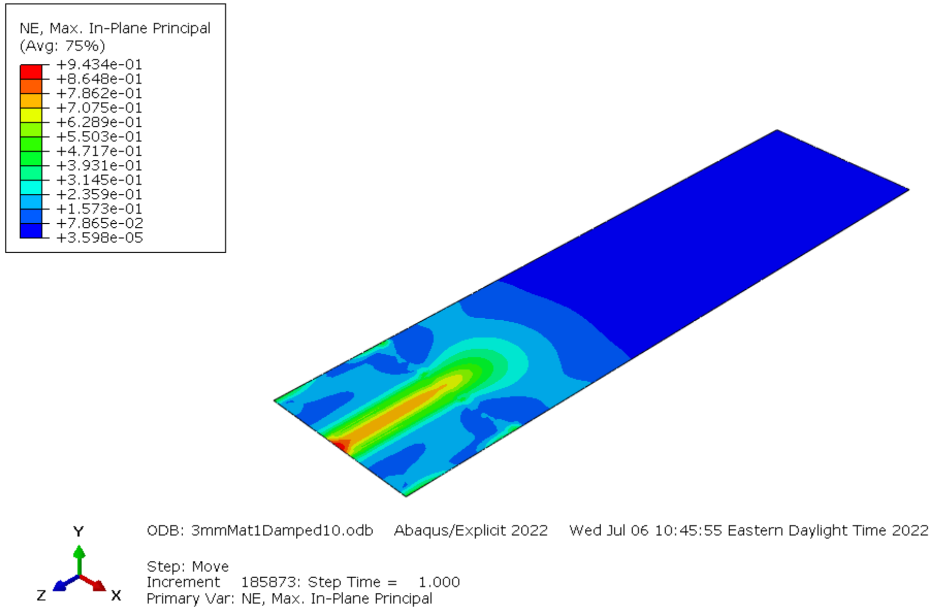
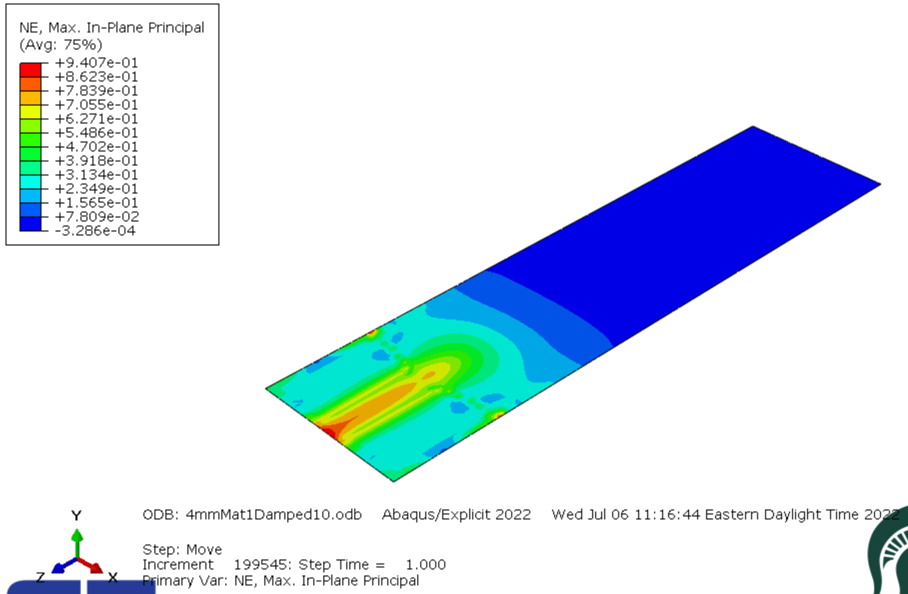
Effect of Thickness



2mm	3mm
	4mm





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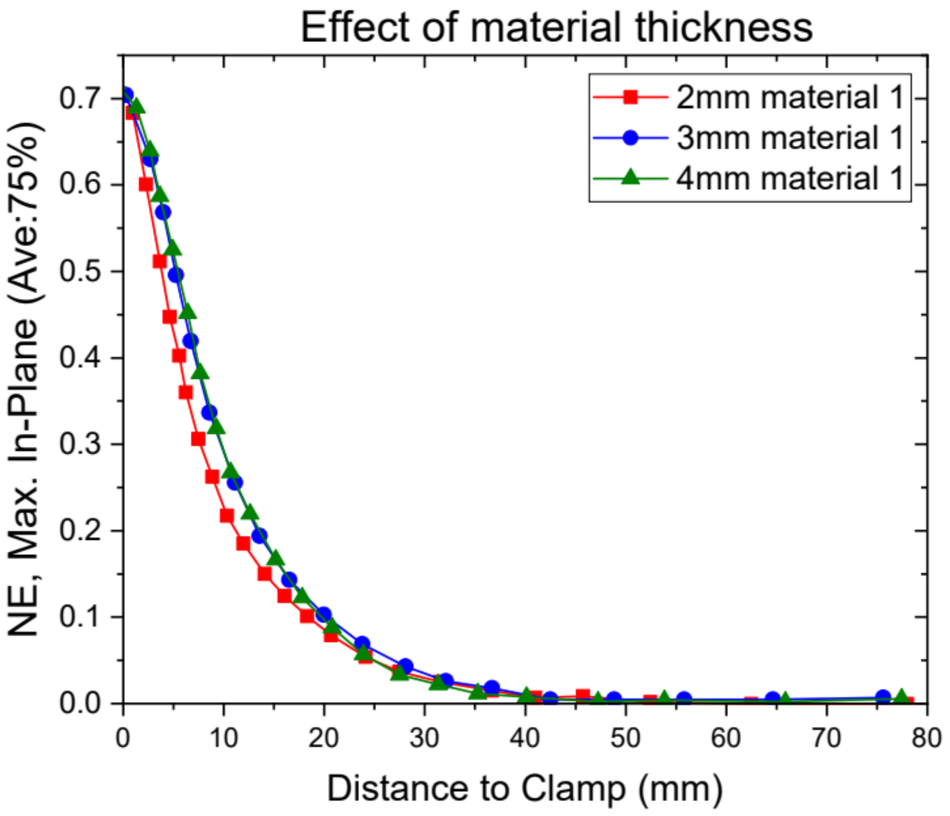
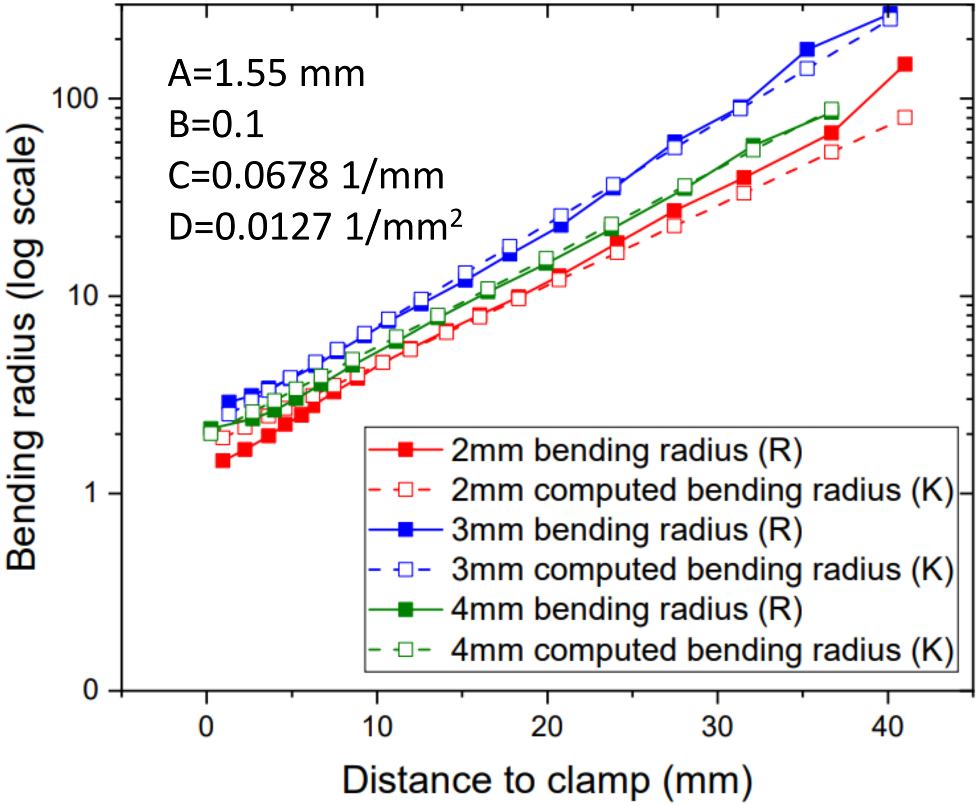
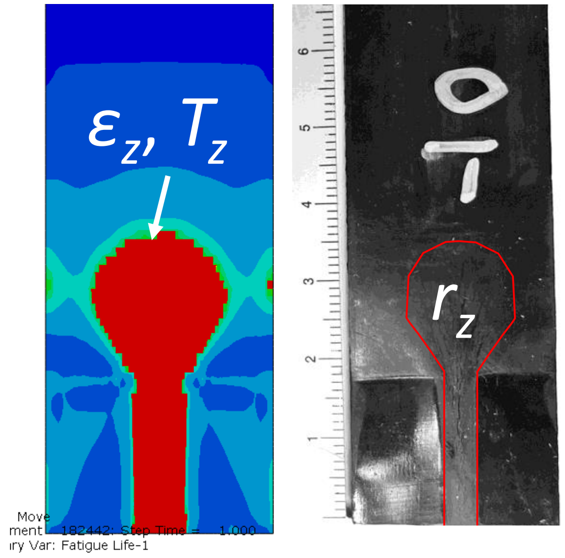
Effect of thickness

$$\varepsilon = \frac{t}{2R} \qquad R = (A + Bt)e^{(C+Dt)X}$$

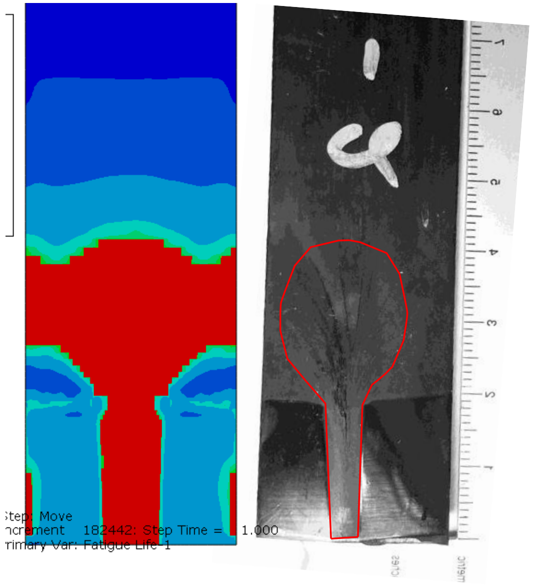




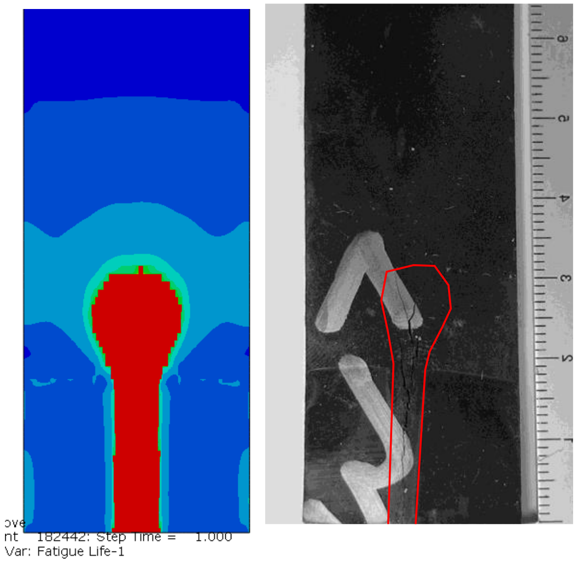
Comparison to experimental results



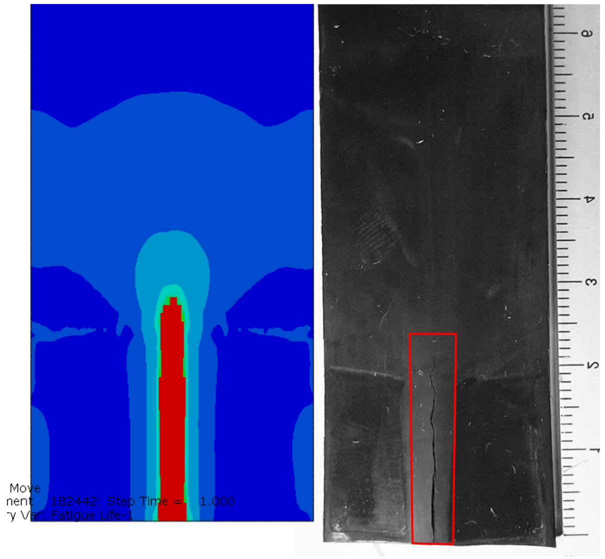
Material 1
T_z = 0.2 J/m^2



Material 2
T_z = 0.1 J/m^2

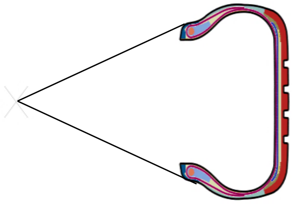


Material 3
T_z = 0.4 J/m^2



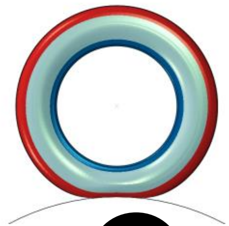
Material 4
T_z = 3.0 J/m^2

Sidewall Cracking Workflow – Global



1

Build **axisymmetric** model and run inflation analysis.

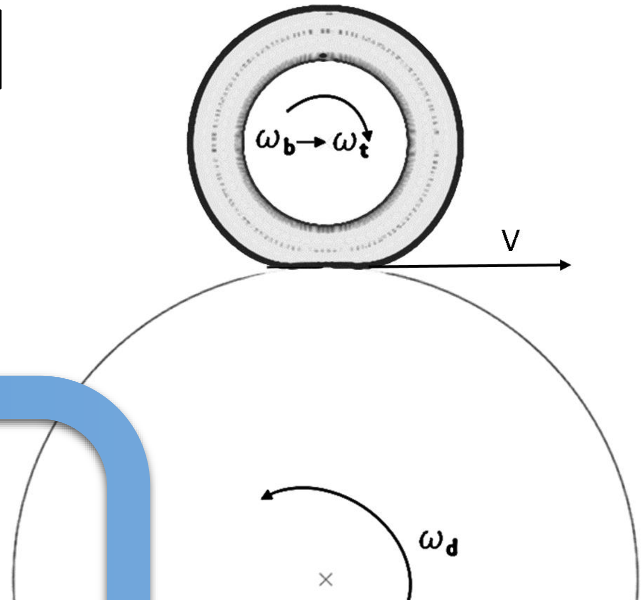


2

Use **Symmetric Model Generation** and **Symmetric Results Transfer** to create a full 3D model. Add drum/flat surface. Run footprint analysis.

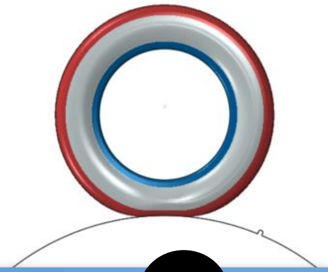
3

Run **Steady-State Transport** analysis. Sweep through the full braking ω_b to the full traction ω_t speed. Calculate the free rolling speed ω_f



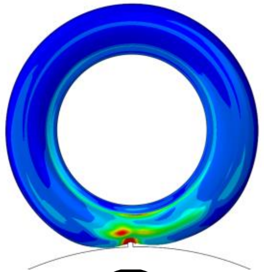
4

Rerun the Steady-State Transport at the **free rolling speed ω_f**



5

Import Steady State Transport results to **Abaqus Explicit.**



6

Run explicit transient

To local model workflow

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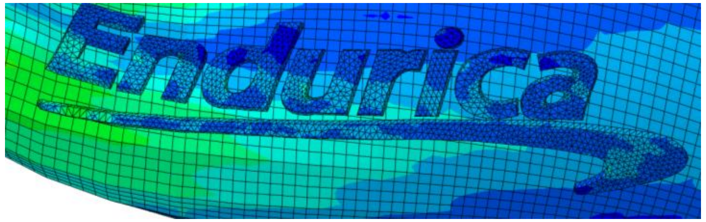
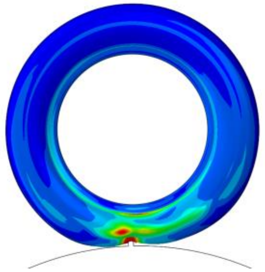
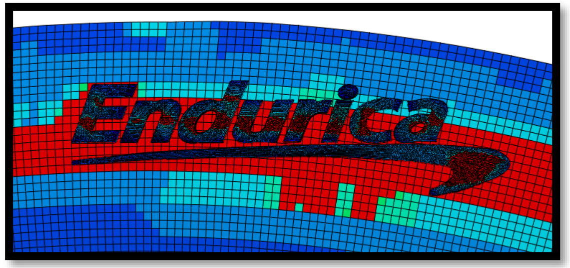
Sidewall Cracking Workflow - Local

Size: P195/75R17
Inflation: 220 kpa
Load: 85% T&RA
Steady State Rolling
One Revolution Per Cycle







1. Build **local model** by tieing 3D letter geometry to membrane model of sidewall surface.
2. Run **transient global/local analysis** thru 1 rev with local model slaved to global tire solution.
3. **Ozone / Fatigue Analysis** of 1 rev of strain history on local model with Endurica CL

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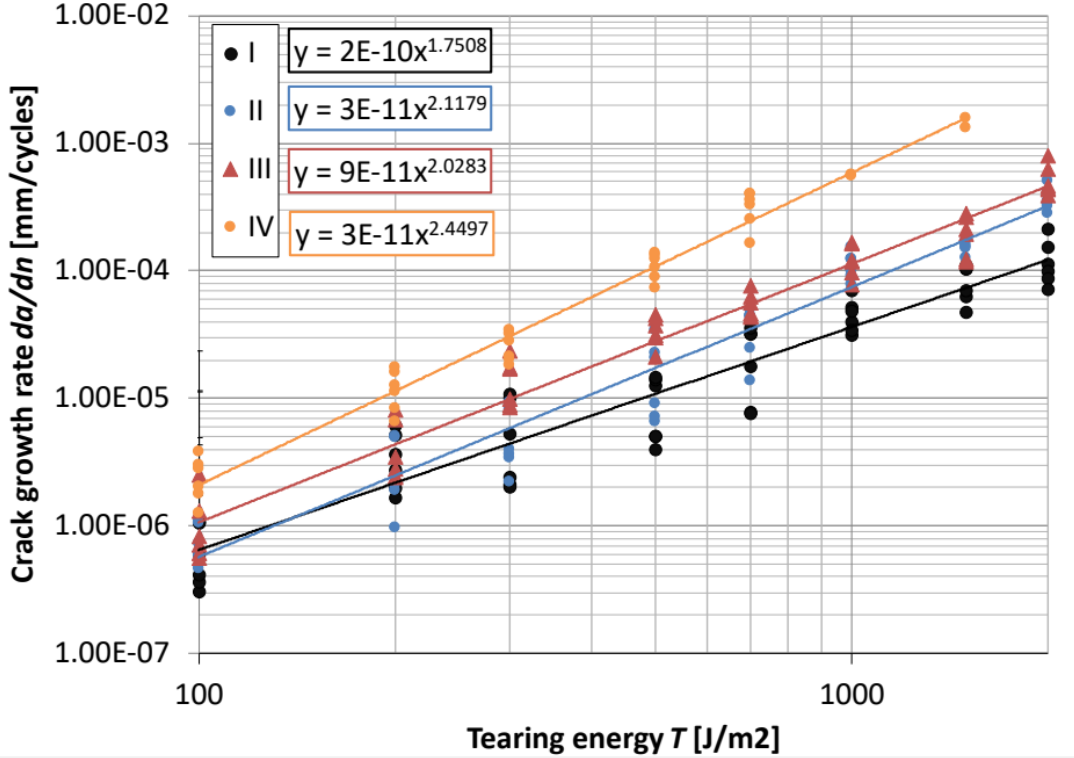
Fatigue Properties

Endurica is the Americas distributor for COESFELD MATERIALTEST



	1	2	3	4
Tc	86.9	13.3	17.0	9.5
Rc	0.00052	0.0017	0.0024	0.037
F0	1.75	2.12	2.03	2.45
T0	0.033	0.020	0.019	0.020

Thank you to Radek Stocek of PRL for the TFA measurements. ISA measurements conducted by ACE.

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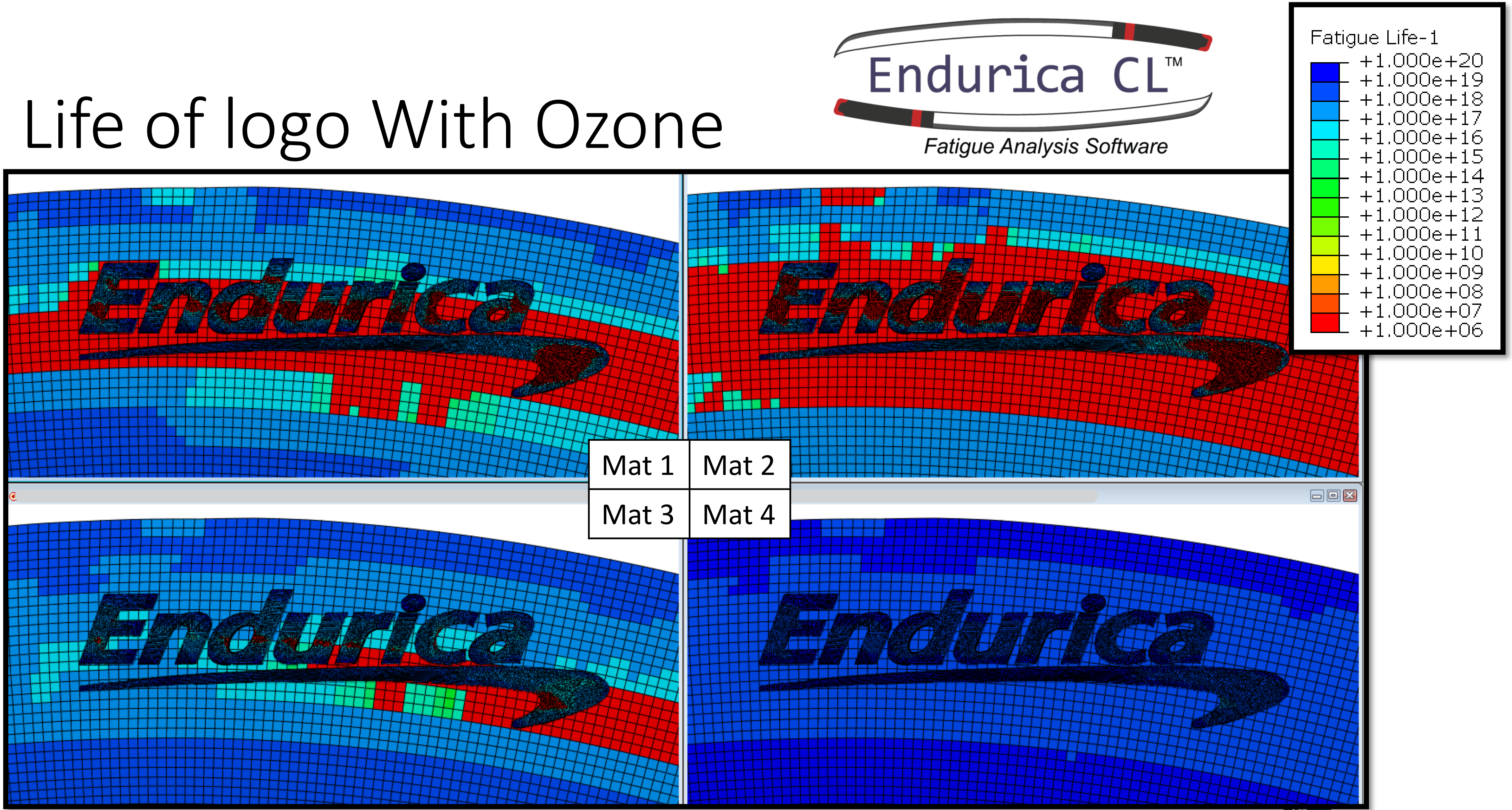
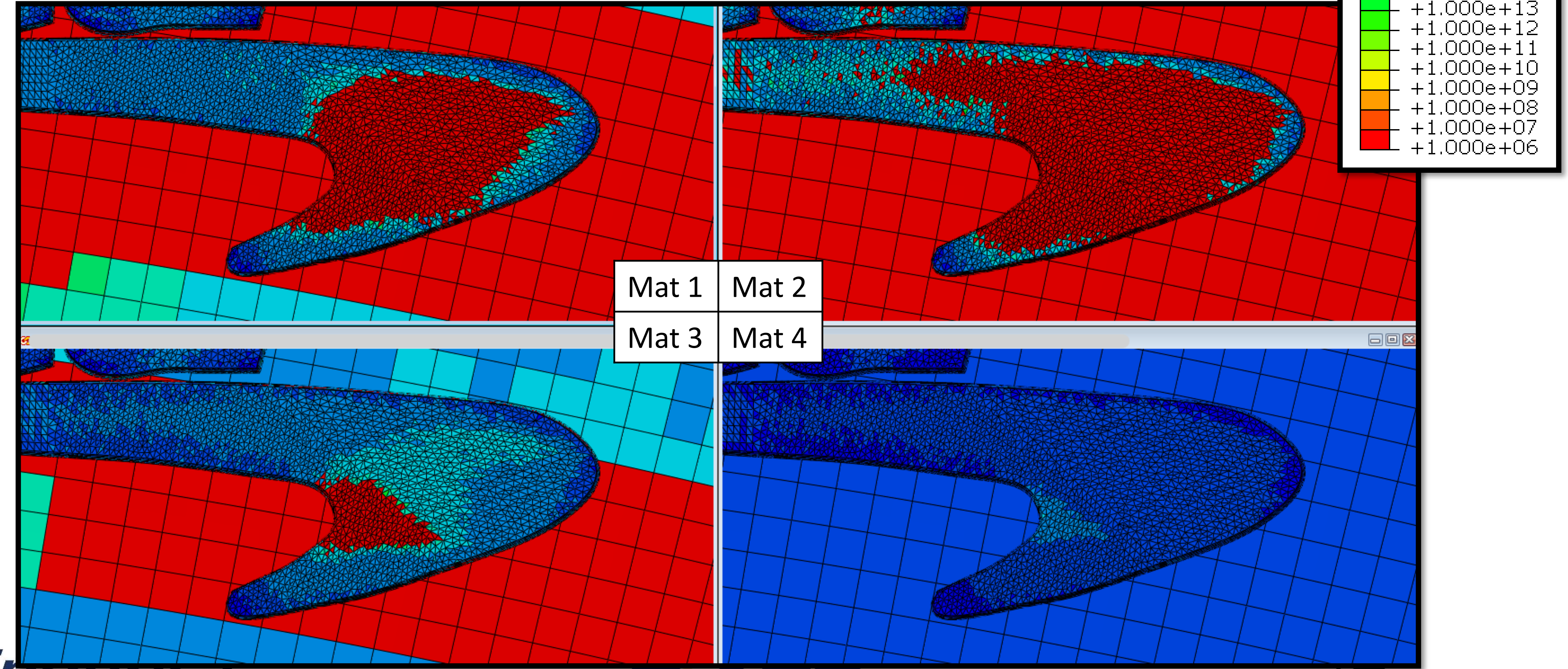
Life of logo With Ozone



Mat 1	Mat 2
Mat 3	Mat 4

Life of logo With Ozone



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Life of logo With Ozone

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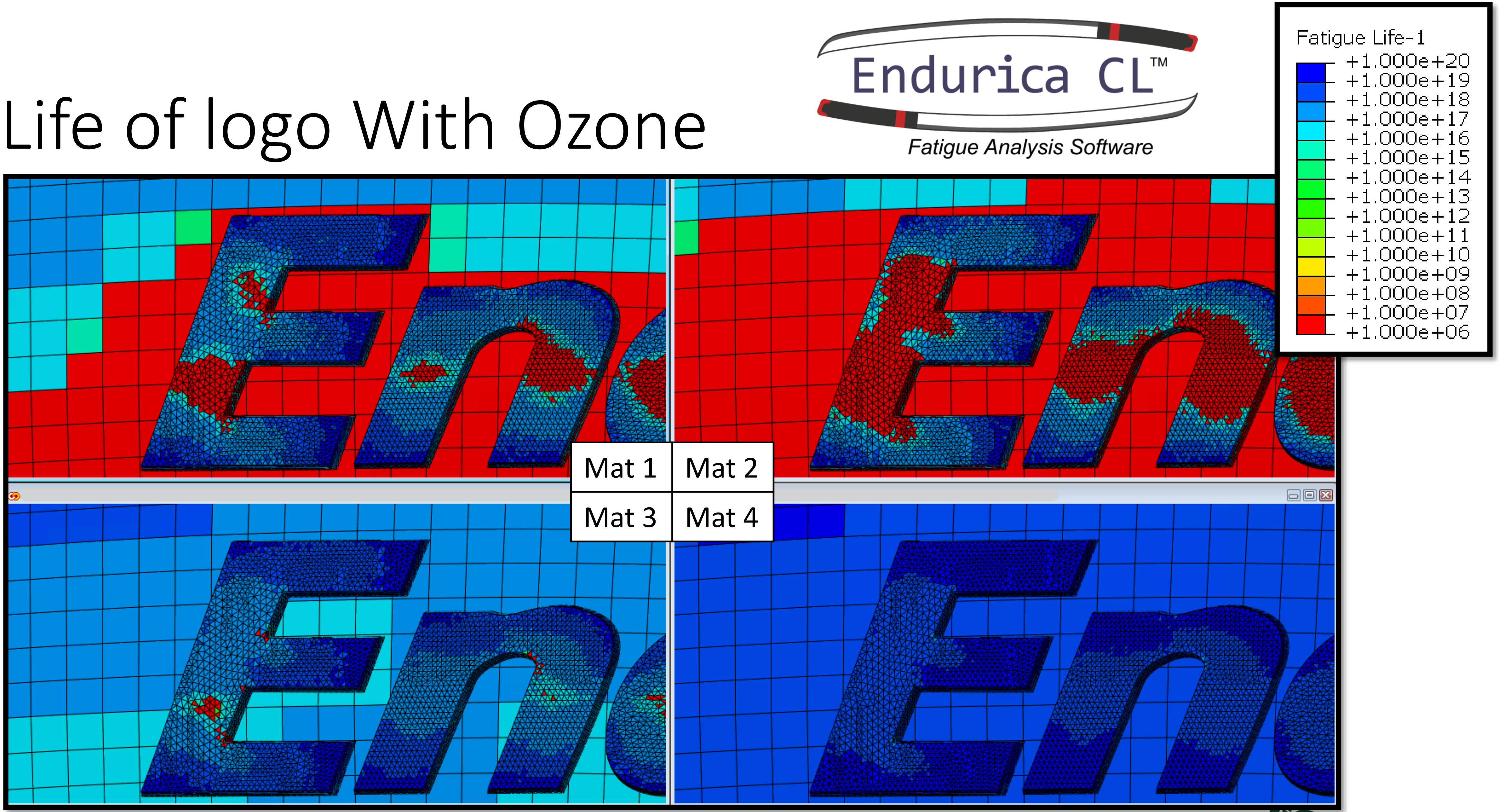

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Summary

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- Elastomers containing C=C bonds (NR) are susceptible to ozone attack
  - Increasing EPDM fraction decreases rz and increases Tz
- Use the Endurica Ozone test to determine Tz and rz
- Use Endurica CL/DT to simulate combined effects of fatigue and ozone attack
- Ensure adequate resistance to ozone attack by simulating letter or groove geometry
- Applications: Tread Groove cracking, Sidewall feature cracking
- Future Work: consider precursor size distribution

Q&A

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Abstract

- Tire sidewall durability depends on specifying compounds with sufficient resistance to fatigue crack growth and to ozone attack. Here the suitability of a series of NR/EPDM blends was evaluated via characterization and simulation. Fatigue crack growth properties were estimated from measurements of intrinsic strength and tear strength made with the Coesfeld Intrinsic Strength Analyzer. Ozone attack threshold and rate were obtained via observations of crack development following exposure in an ozone chamber. The ozone attack measurements also provide information about the distribution of crack precursors in each compound. Finally, using FEA-computed sidewall strain history for steady rolling, estimates were made of sidewall life and likely distribution of cracking.

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