Optimizing Solution Chemistry for Reduced Damage during CMP

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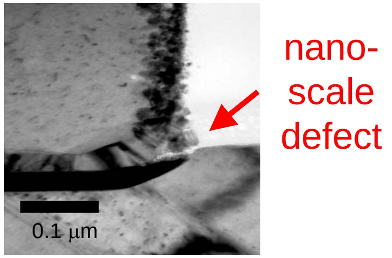
Evolution of Defects control Yield through Processing

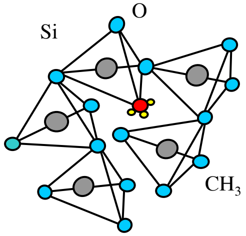
- <u>Lower</u> driving force for cracking, G_{total}

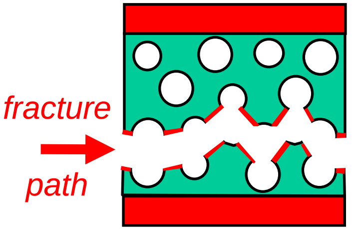


  - thin film stresses
  - CMP stresses

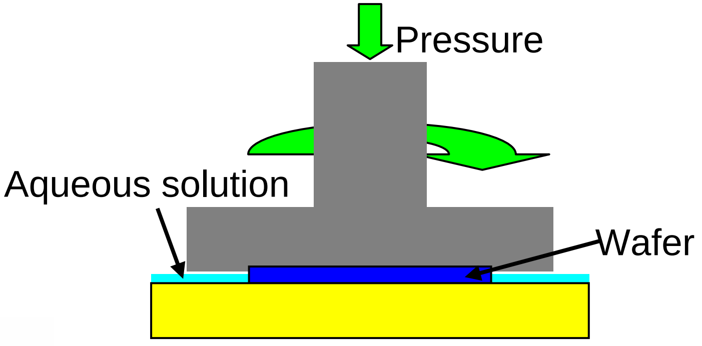
$$G_{total} \leq G_c \ (J/m^2)$$

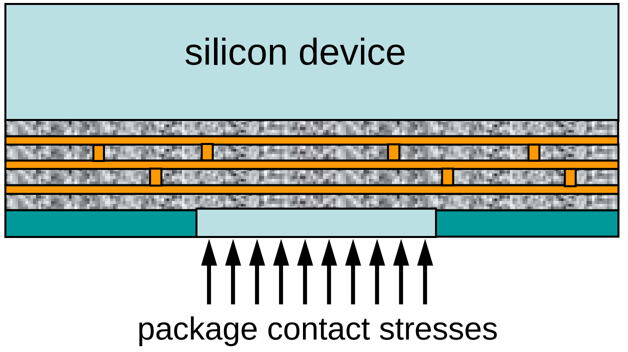
- <u>Optimize</u> resistance to cracking - glass composition, network and pore structure





- <u>Control evolution</u> of defects during processing, packaging and service





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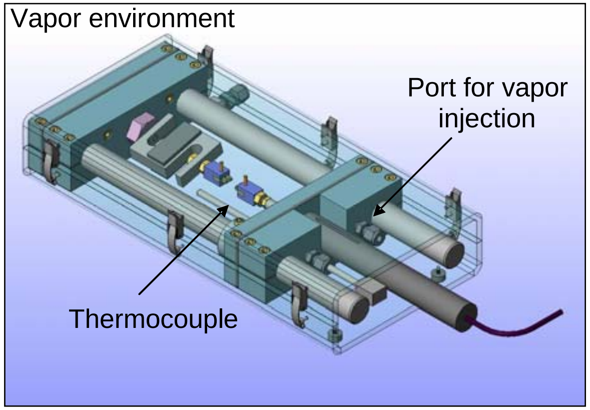
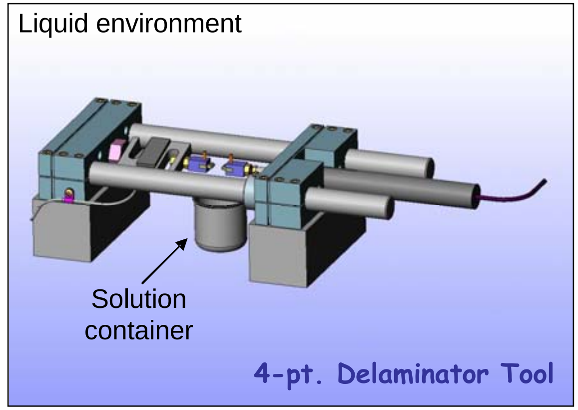
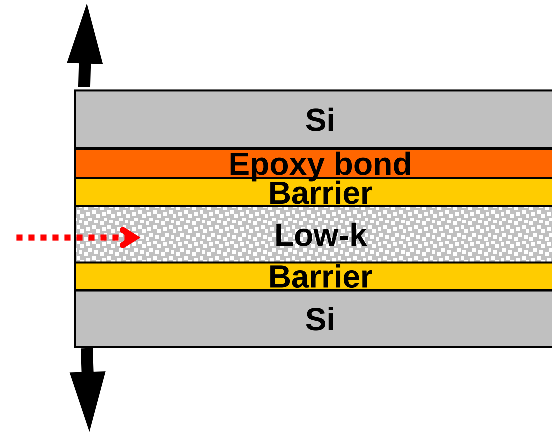
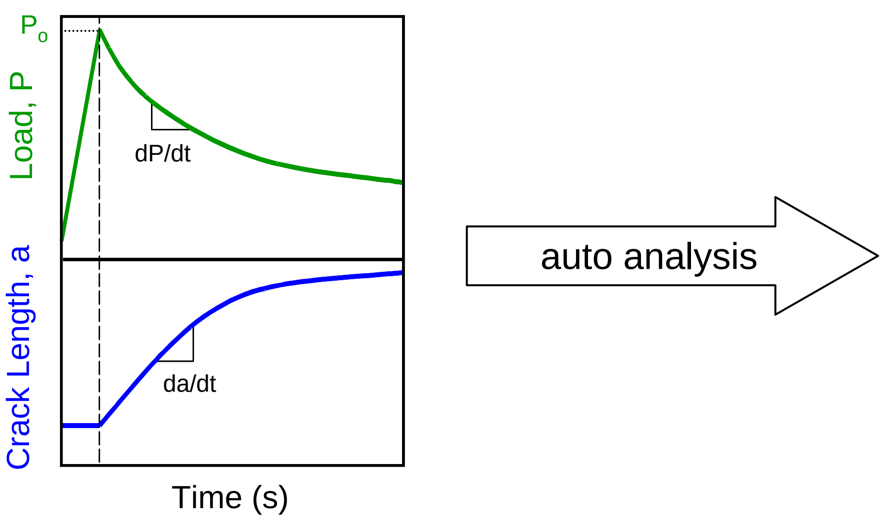
Automated Crack Velocity Testing

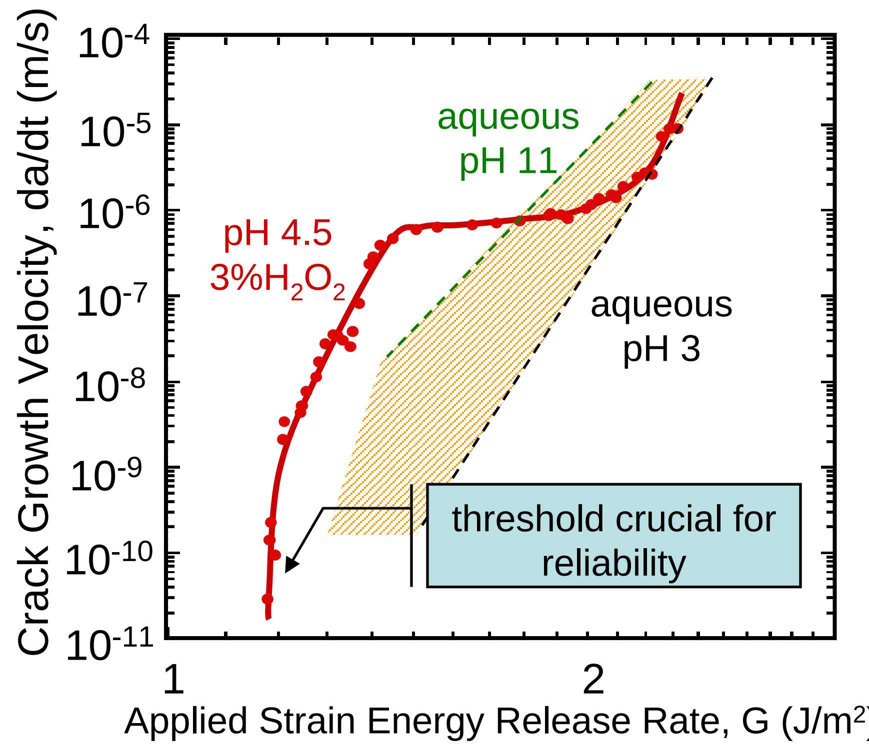






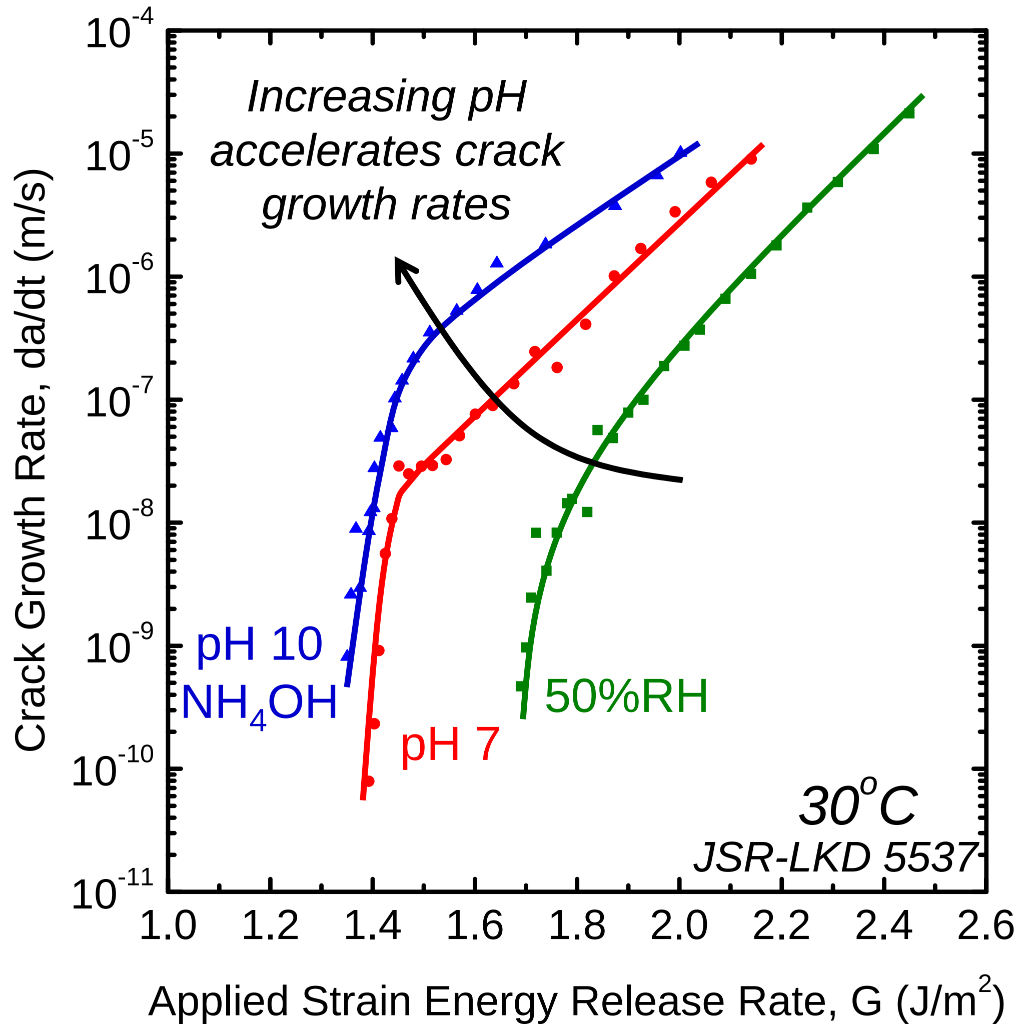
Load Relaxation Crack Growth Technique

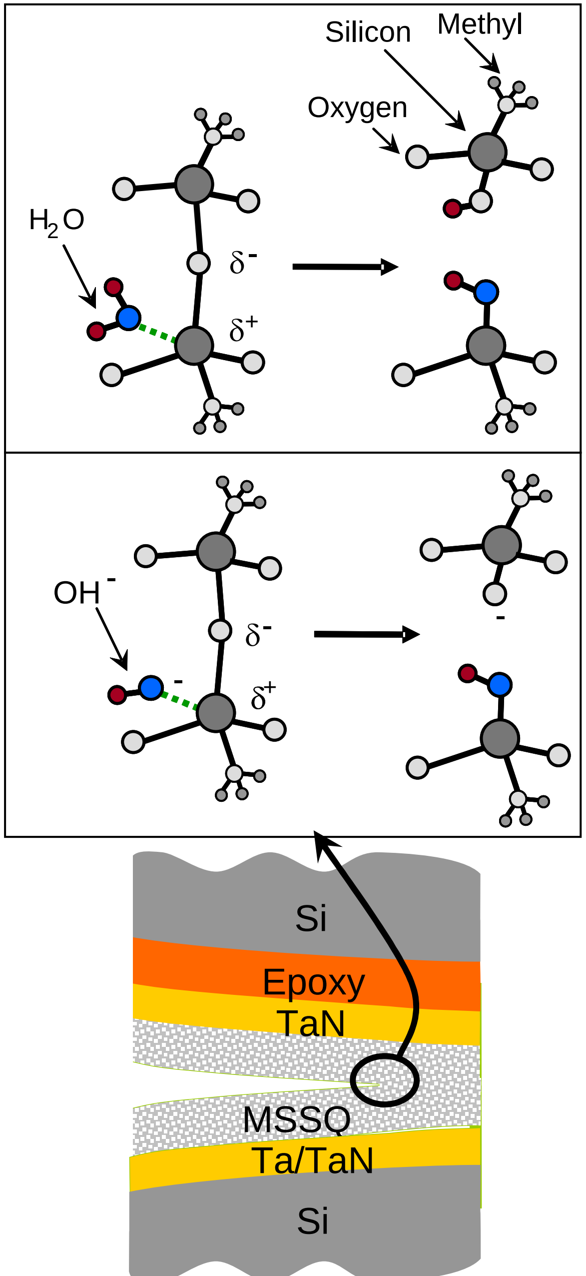




System and support:
DTS Company, Menlo Park, CA (dauskardt@stanford.edu)

Effects of Solution pH on Crack Growth





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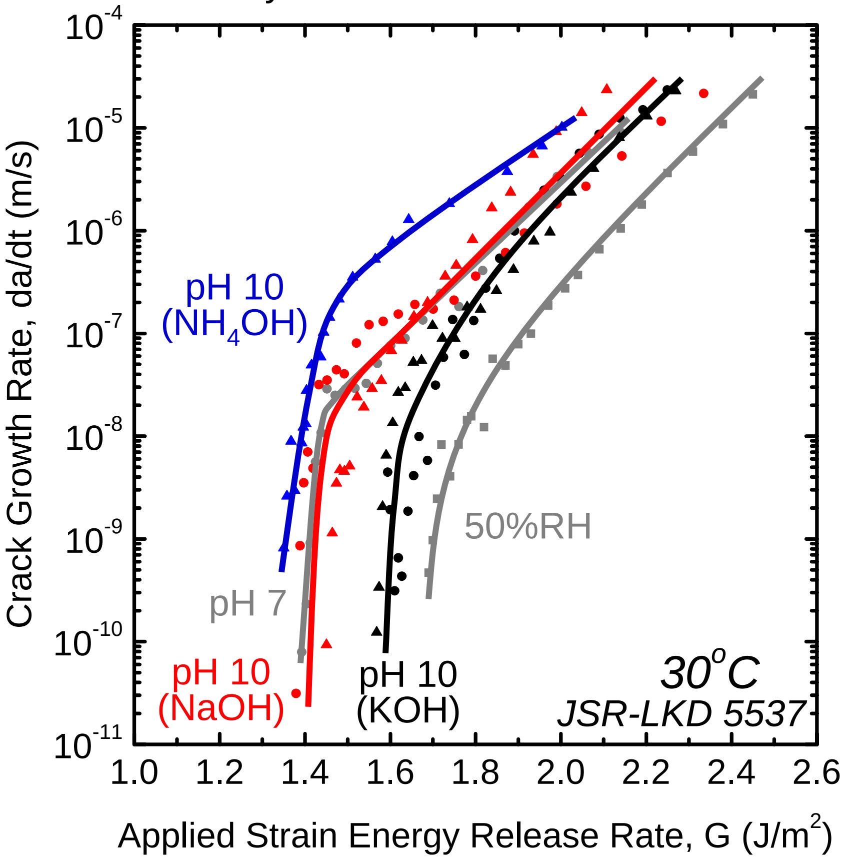
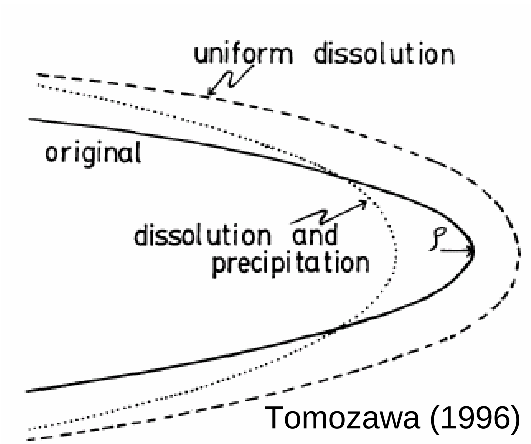
Alkali metal ion + crack tip →
decelerated crack growth by crack tip blunting

Electrolytes in DI water w/o surfactants



Crack tip gets blunted by dissolution of the silica backbone.



Inglis expression for the stress concentration

$$\sigma_t = 2\sigma\sqrt{a/\rho}$$

Silica gel dissolution in aqueous alkali metal hydroxides

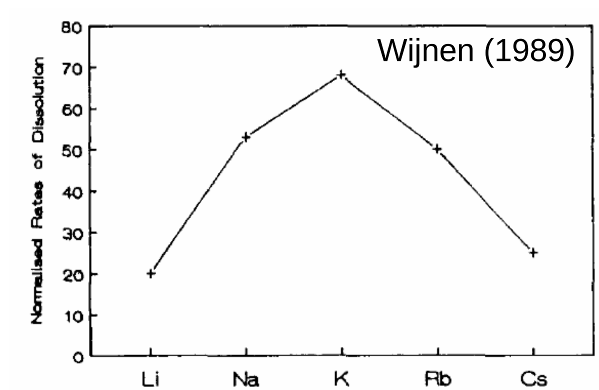


Fig. 5. Normalised rate of dissolution, obtained from ^{29}Si–NMR spectra, as a function of alkali metal hydroxide.

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Effects of Nonionic Surfactants on Defect Evolution during CMP

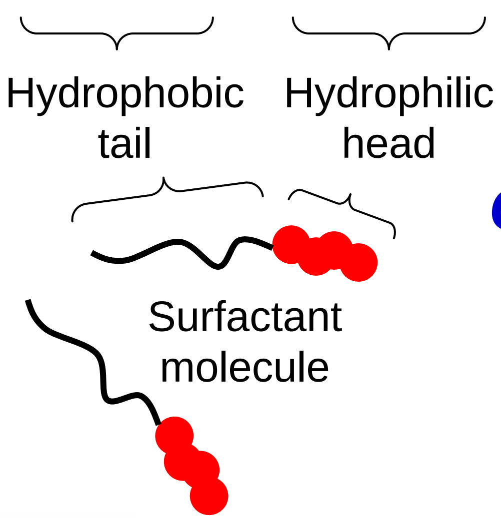
Surfactant additions critical for efficient CMP:

- enhances wetting of hydrophobic low-k dielectrics
- stabilizes CMP slurry
- optimized CMP removal rates, reduced dishing…

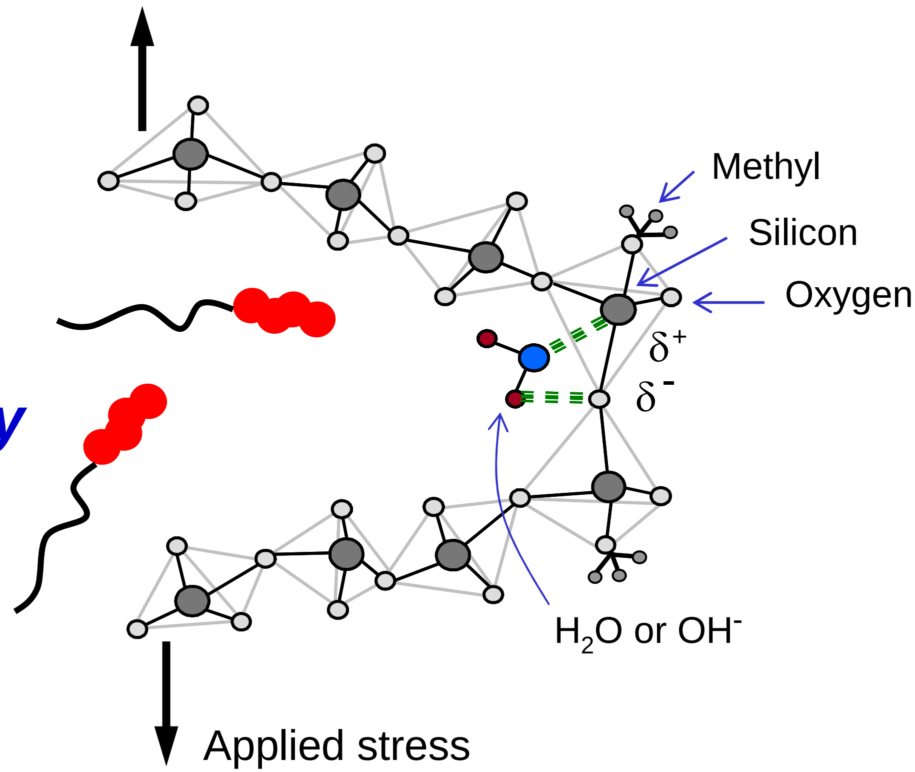
Effects of surfactant molecules on the defect evolution/crack growth are unknown!

polyoxyethylene alkyl ether

$CH_3(CH_2)_{m\text{-}1}O(CH_2CH_2O)_nH$



CMP slurry



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Nonionic Surfactants: Polyoxyethylene Alkyl Ethers

Monomeric surfactant

$CH_3(CH_2)_{m\text{-}1}O(CH_2CH_2O)_nH$ ⇒ C_mE_n

Hydrophobic hydrocarbon chain

Hydrophilic ethylene oxide (EO) chain

Commercial name	# of C, *m*	# of EO, *n*	HLB	Molecular weight (g/mol)	Molarity of 0.1wt% surfactant solution (M)
ETHALL DA-4	10	4	10.5	334	2.99×10^{-3}
DA-6		6	12.4	423	2.37×10^{-3}
DA-9		9	14.3	555	1.80×10^{-3}
ETHALL LA-4	12	4	9.2	363	2.76×10^{-3}
LA-7		7	12.2	495	2.02×10^{-3}
LA-23		23	16.8	1200	8.34×10^{-4}
LA-50		50	18.3	2389	4.19×10^{-4}
BRIJ 76	18	10	12.4	711	1.41×10^{-3}
78		20	15.3	1152	8.68×10^{-4}
700		100	18.8	4676	2.14×10^{-4}

Hydrophilic-Lipophilic Balance (HLB)

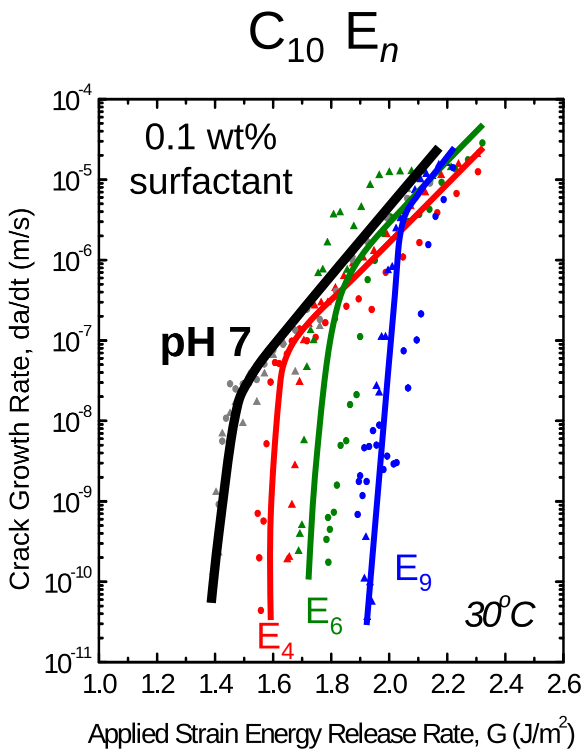
lipophilic	1	20	hydrophilic
(oil soluble)	←	→	(water soluble)

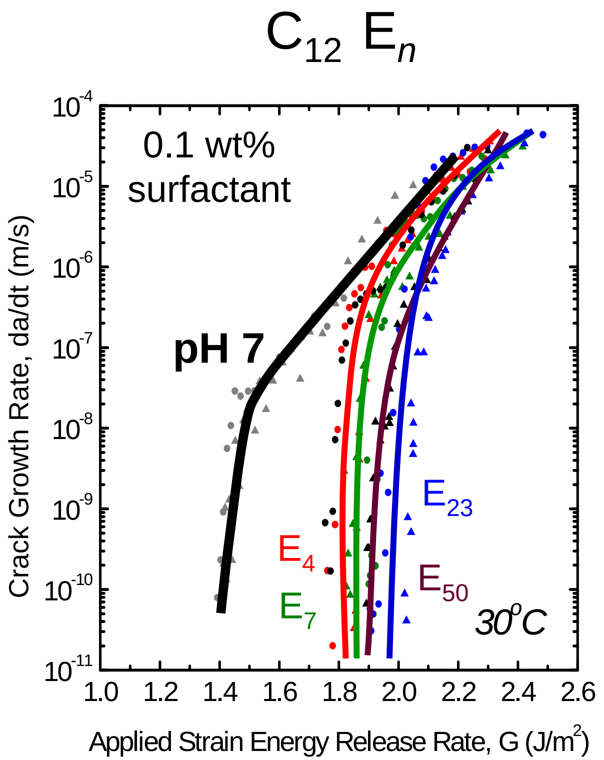
CMC @25 ℃

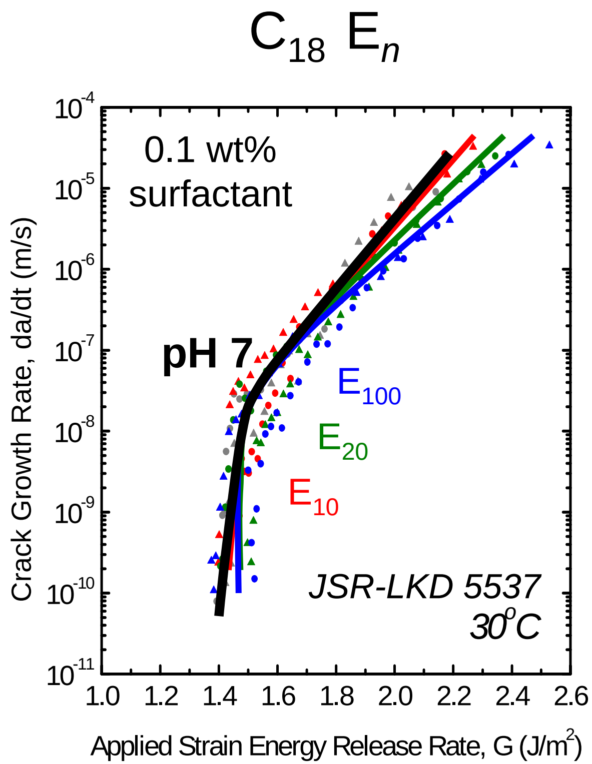
BRIJ 76: 4×10^{-3} wt%

BRIJ 78: 9.5×10^{-4} wt%

C_mE_n Effects on Crack Growth Behavior (in pH 7 NH_4OH)



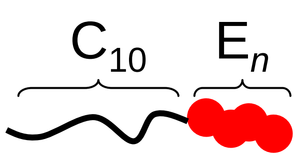


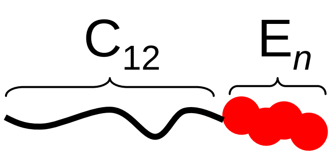


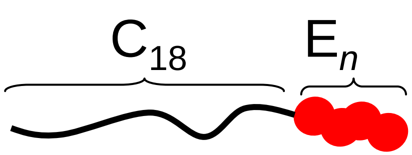
Marked effect on crack growth
Sensitive to hydrophilic chain length

Marked effect on crack growth
Insensitive to hydrophilic chain length

No effect of surfactant molecules







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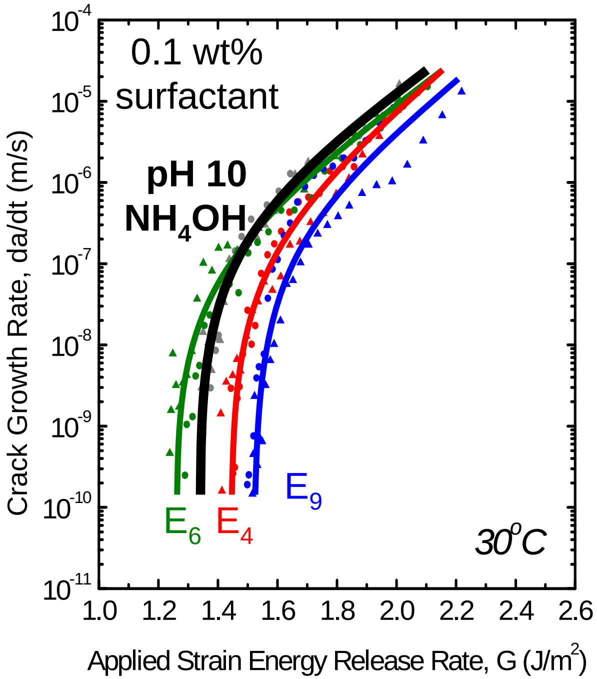
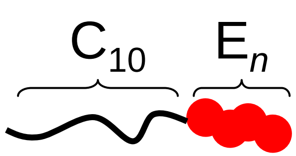
C_mE_n Effects on Crack Growth Behavior (in pH 10 NH_4OH)

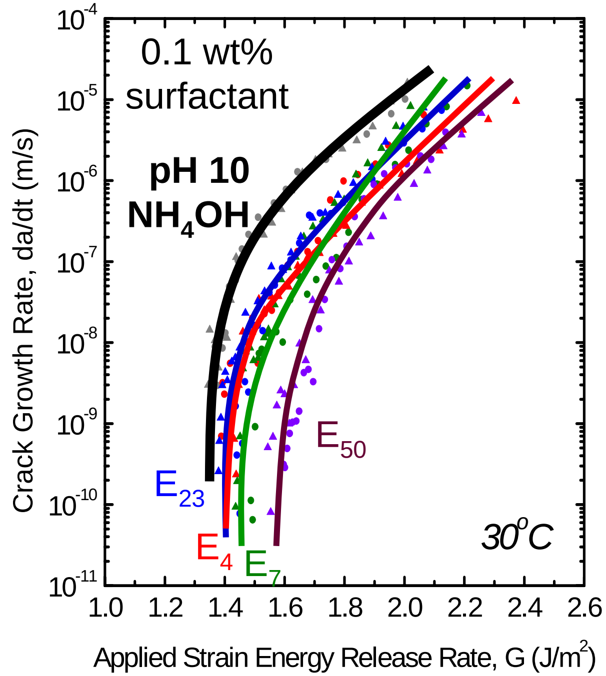
C_{10} E_n



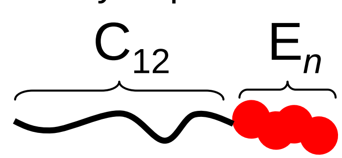
Little effect of surfactant molecules



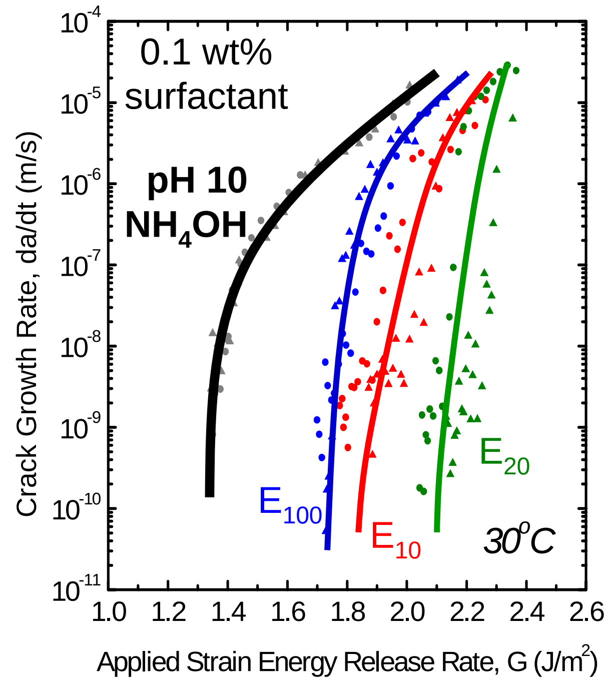
C_{12} E_n



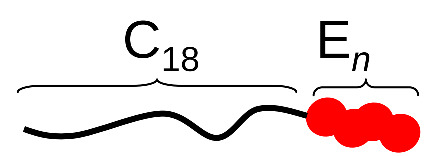
some effect on crack growth
Insensitive to hydrophilic chain length



C_{18} E_n



Marked effect on crack growth
Sensitive to hydrophilic chain length



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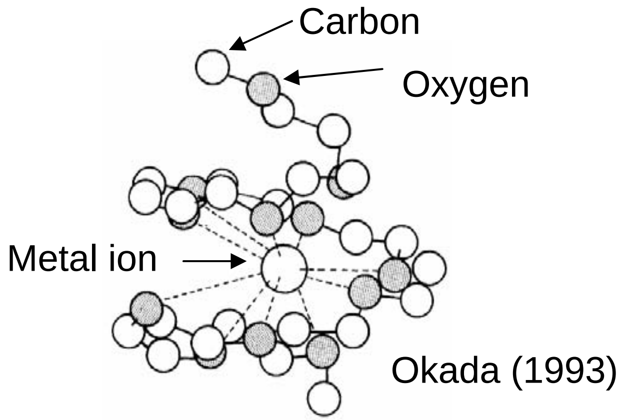
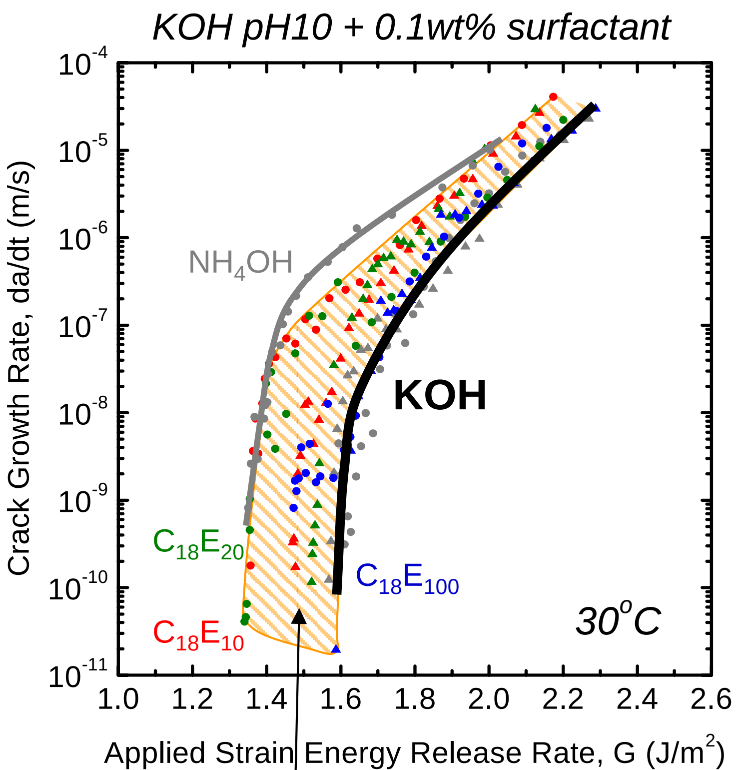
C_mE_n Effects on Crack Growth Behavior (in pH 10 KOH)

Alkali metal ion + EO → Complexation

EO of Polyoxyethylene Alkyl Ether



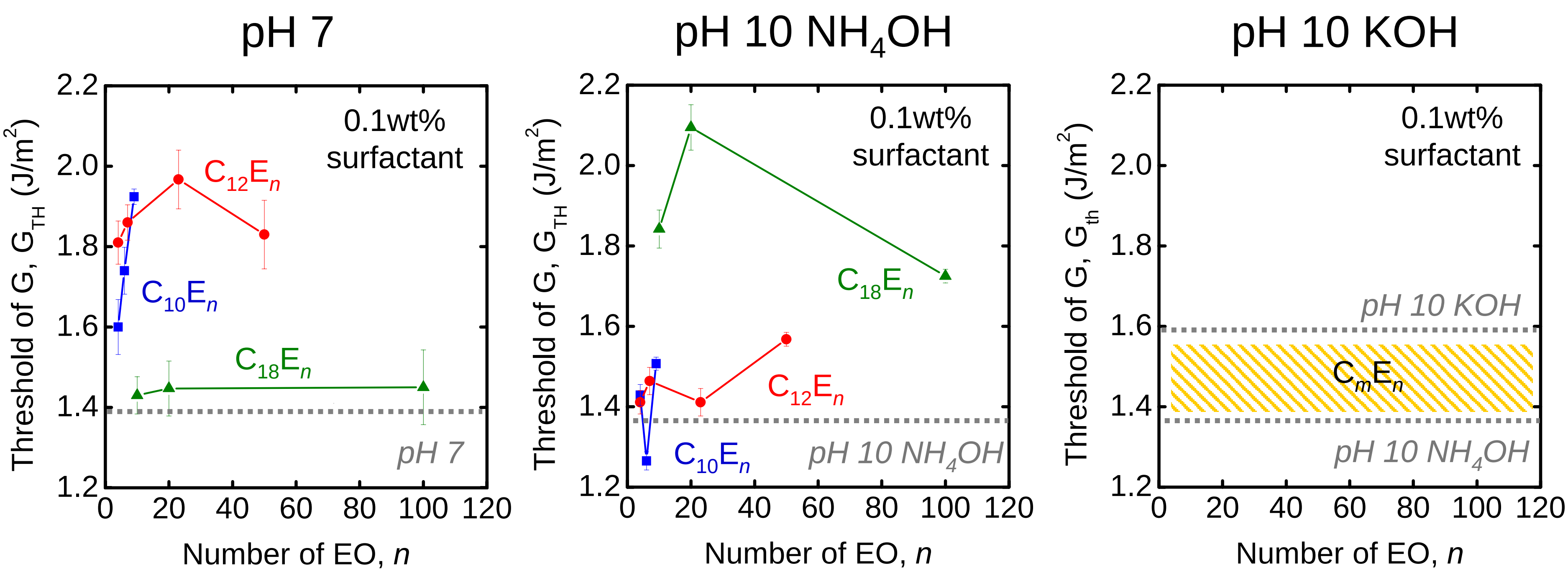
The EO chain locked by the cation, stabilzed by electron-rich oxygen atoms, decreases mobility



Crack tip blunting effects suppressed by shielding of potassium ion.

Also, complexation reduces hydrogen bonding sites ↓→ $G_{bridging}$ ↓

Threshold Applied Strain Release Rate (C_mE_n)



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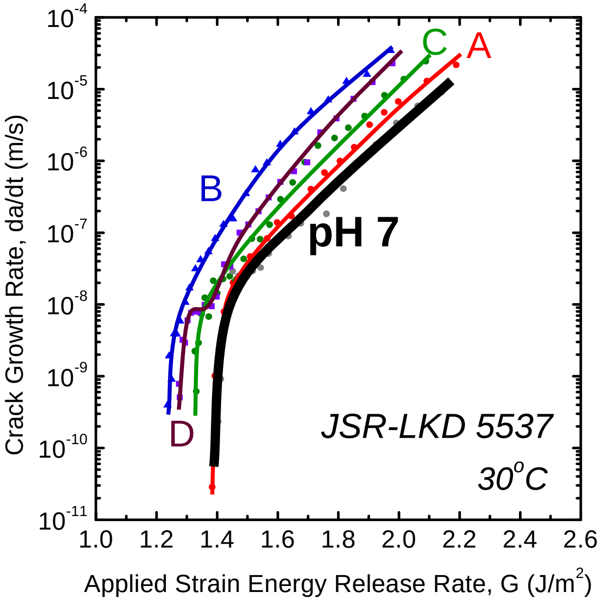
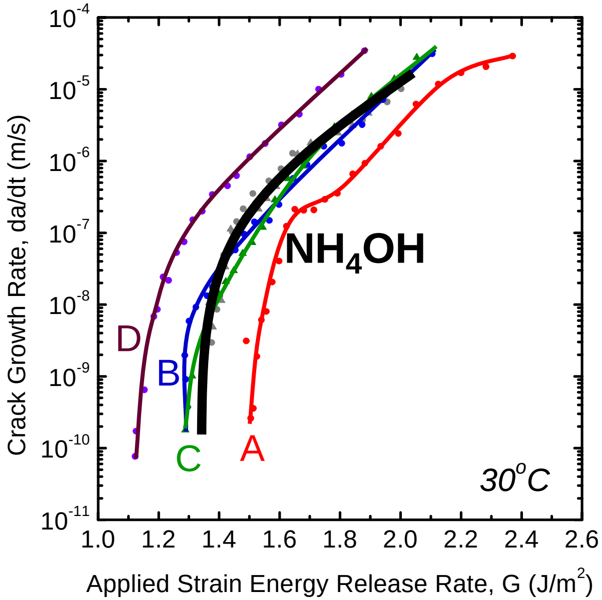
Nonionic Gemini (Dimeric) Surfactants Effects on Crack Growth Behavior

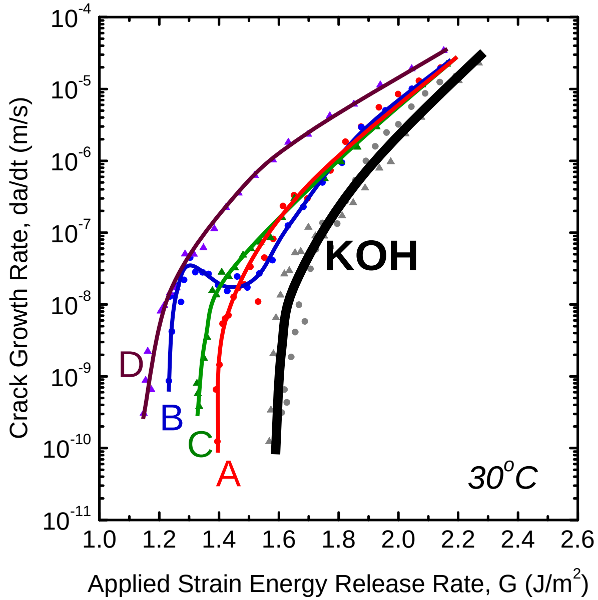
pH 7 + 0.1wt% surfactant



pH10 NH_4OH + 0.1wt% surfactant



pH10 KOH + 0.1wt% surfactant



EO length: A < B < C < D

Low foaming (defoaming) and rapid surface wetting

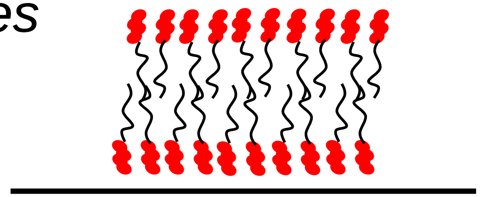
→ accelerated crack growth

Nonionic Surfactants Organization and Interaction with Surfaces

organization into aggregates depends on molecular type, concentration, temperature, pH, ionic content, surfaces, confinement….

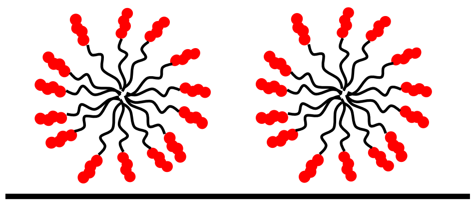
- *C_mE_n*
- *SiO_2 surface binding sites*

small n (large m) — *high*



bi-layer aggregates

large n (small m) — *low*

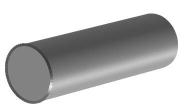


micellar aggregates

- *confinement in cracks or pores*

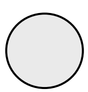
1-D — surface / surface ↕ δ — crack surfaces

2-D



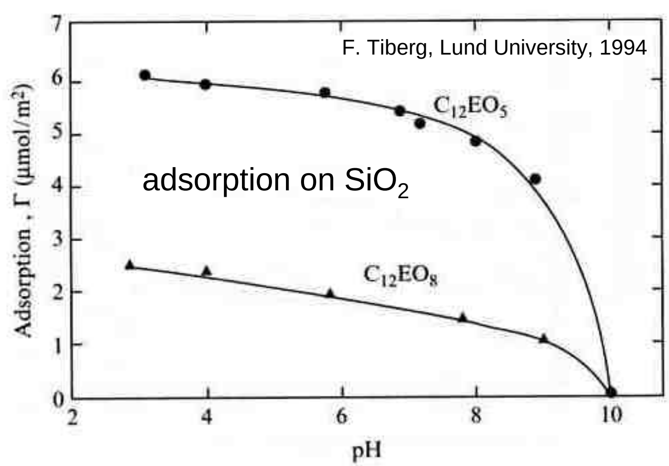
cylindrical pores

3-D



pores

- *pH effects*



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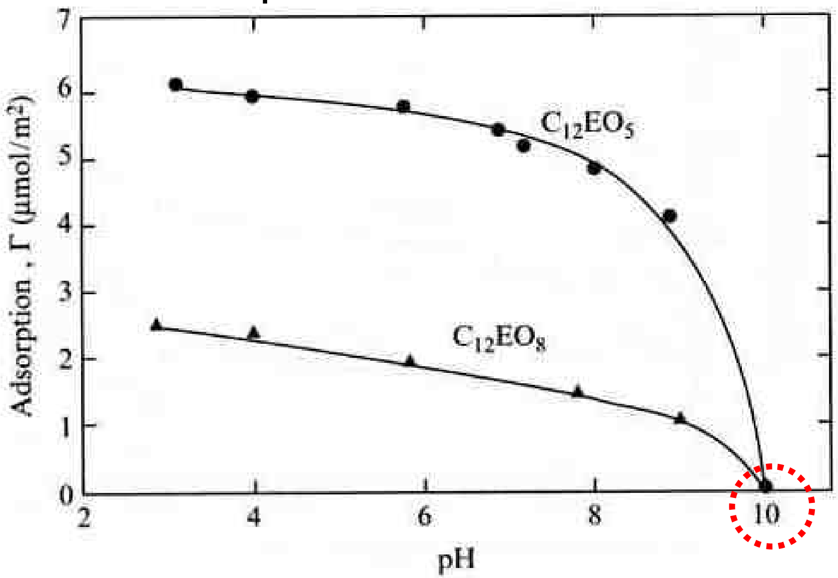
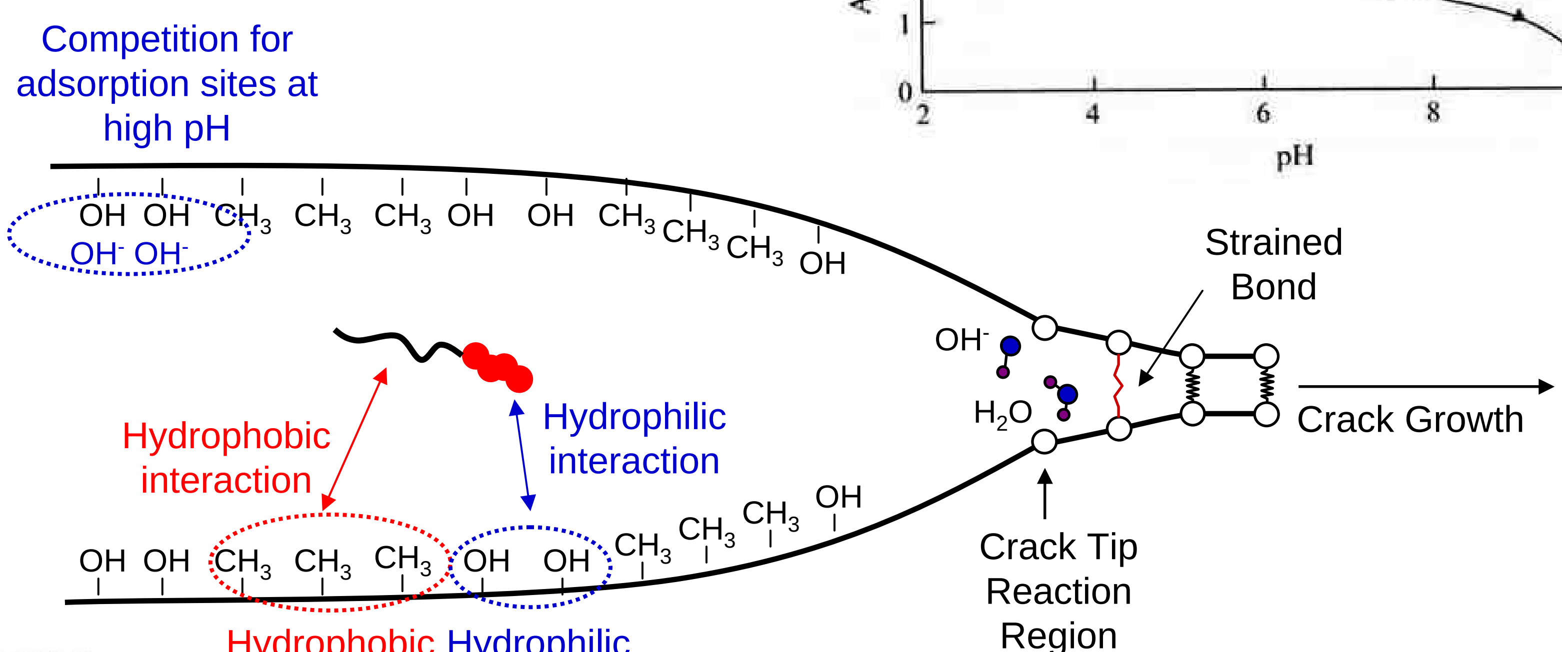
Hydrophobic and Hydrophilic Interactions

Hydroxyl ions from alkaline solution compete for adsorption sites and at pH levels above 10 all surfactants are displaced from the surface.

[F. Tiberg Ph.D. Thesis, Lund University. Sweden, 1994].

Adsorption on the silica surface





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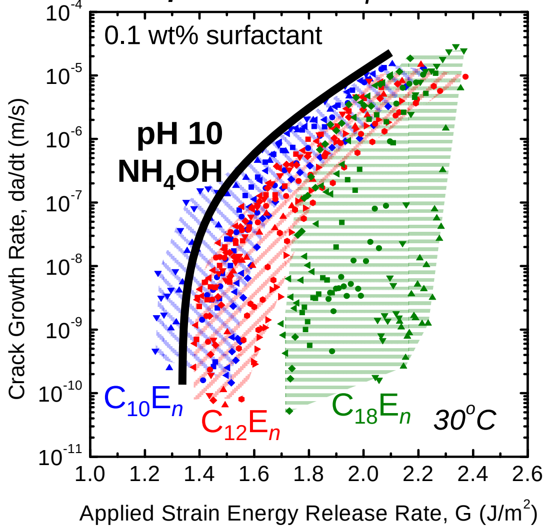
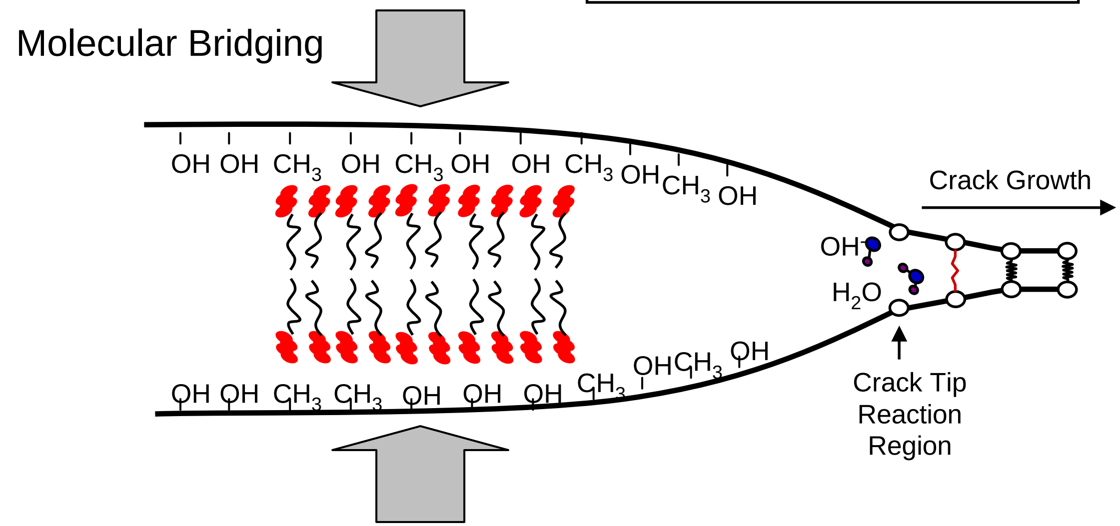
Molecular Bridging in Aqueous Solution

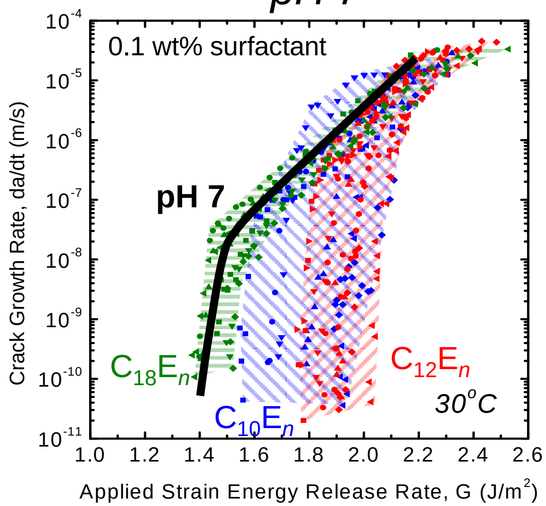
$$G_{tip} = G_{applied} - G_{bridging}$$

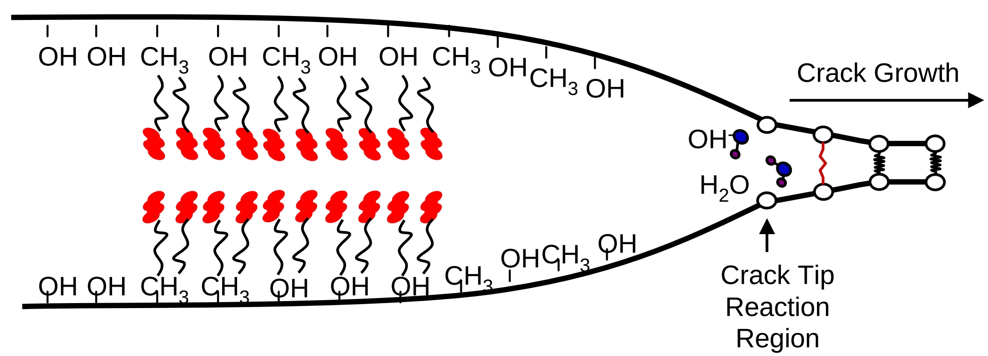
pH 10 NH_4OH



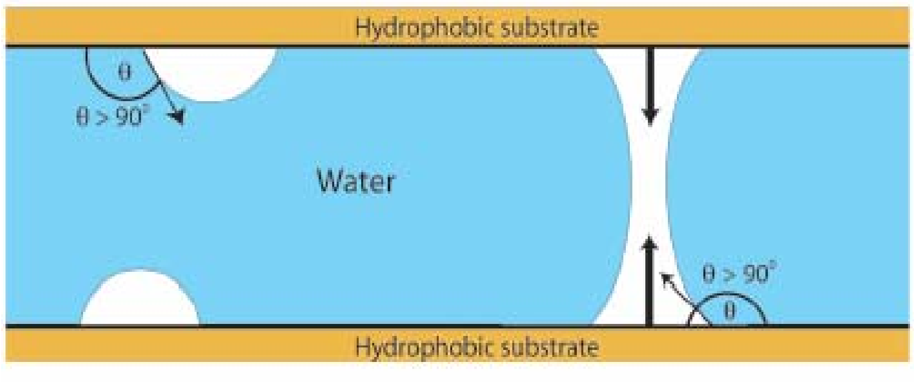


pH 7

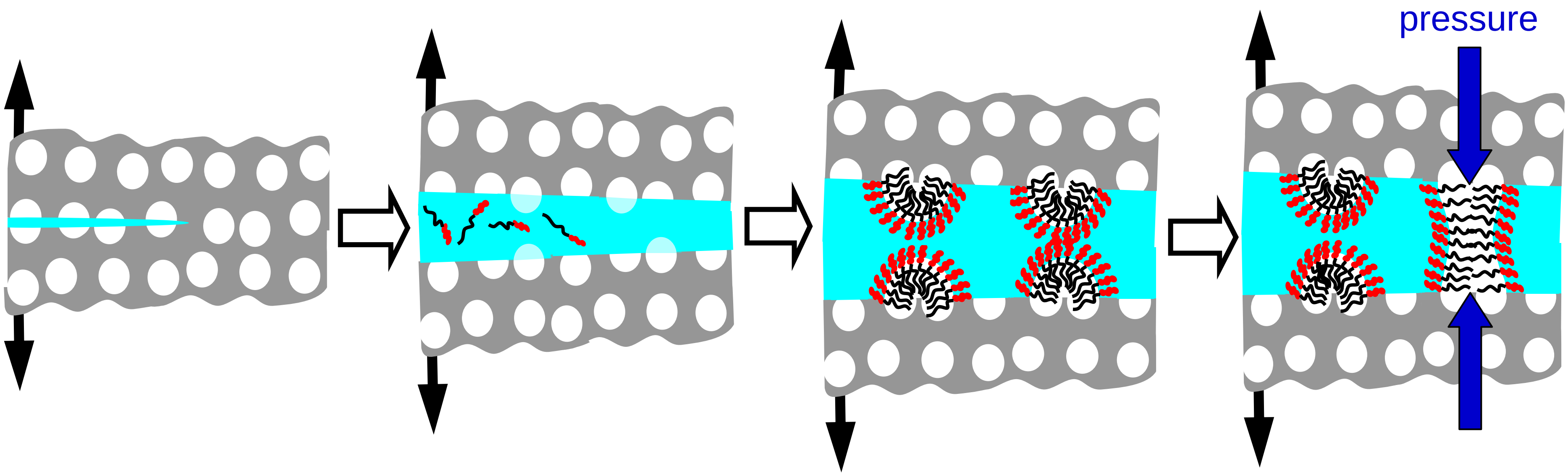




Surfactant-Enhanced Nanobubble Cavitation



When present on hydrophobic surfaces, nanobubbles can coalesce, leading to an attractive Laplace pressure. Adhesion ~ 1.0 J/m^2 was measured for D < 10 nm. [Meyer, Rosenberg, and Israelachvili, 2006]

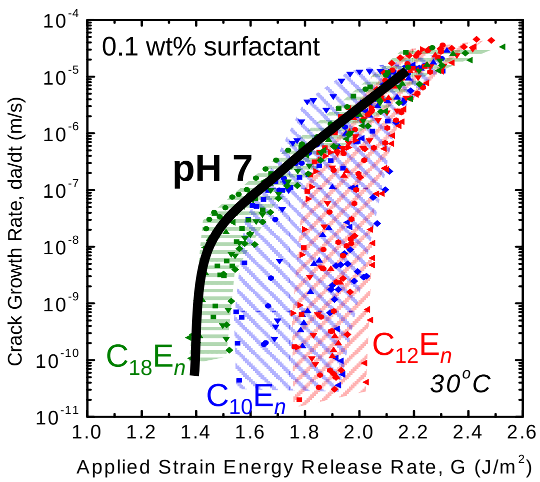


Conclusions

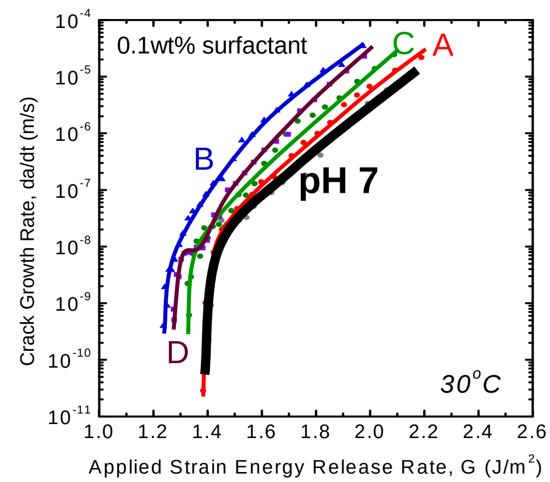
<u>Effects of surfactant additions on the defect evolution</u>

Suppressed crack growth by bridging ⟷ Accelerated crack growth by wetting

Monomeric surfactant:
Polyoxyethylene alkyl ethers



Gemini (dimeric) surfactant



Building a new understanding of the effective CMP slurry formulations for the reliable integration of ultra-low-k materials at next technology nodes.

Q & A