Optimizing Solution Chemistry for Reduced Damage during CMP

April 4, 2007

Taek-Soo Kim[1], Qiping Zhong[2], Maria Peterson[2], Halbert Tam[2], Tomohisa Konno[3], and Reinhold H. Dauskardt[1]

[1]Stanford University, Stanford, CA 94305 USA
[2]JSR Micro, Inc., 1280 N. Mathilda Ave., Sunnyvale, CA 94089, USA
[3]JSR Corporation, Yokkaichi Research Center, 100 Kawajiri-cho, Yokkaichi, Japan

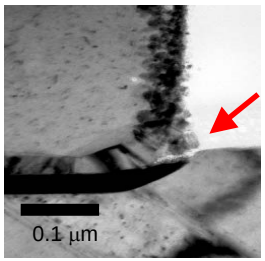
STANFORD ENGINEERING

JSR

JSR Micro JSR MATERIALS INNOVATION

Evolution of Defects control Yield through Processing

- Lower driving force for cracking, G_{total}



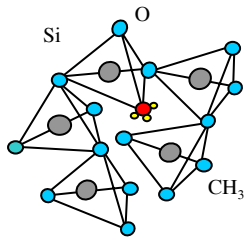
nano-scale defect

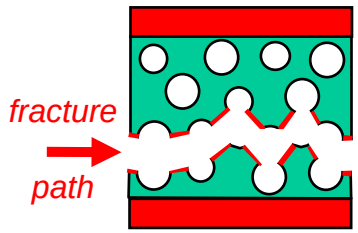
– thin film stresses

– CMP stresses

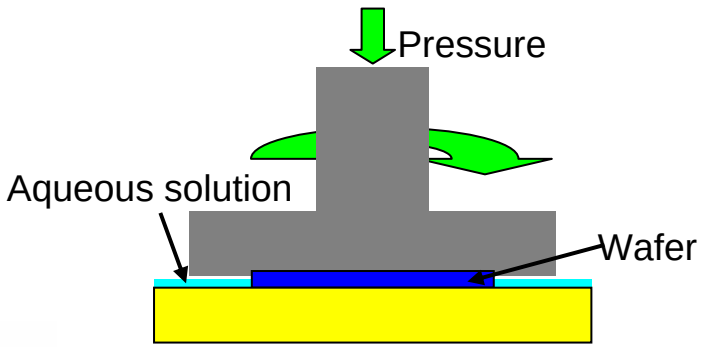
$$G_{total} \leq G_c \ (J/m^2)$$

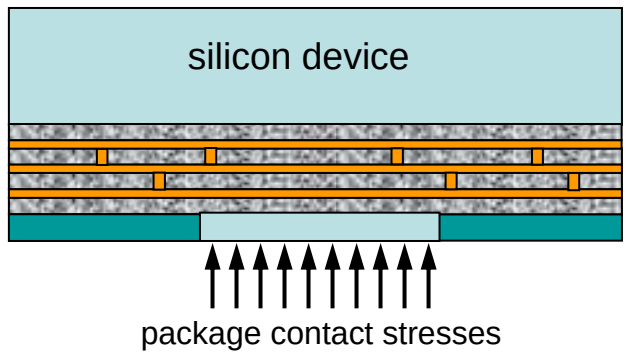
- Optimize resistance to cracking - glass composition, network and pore structure





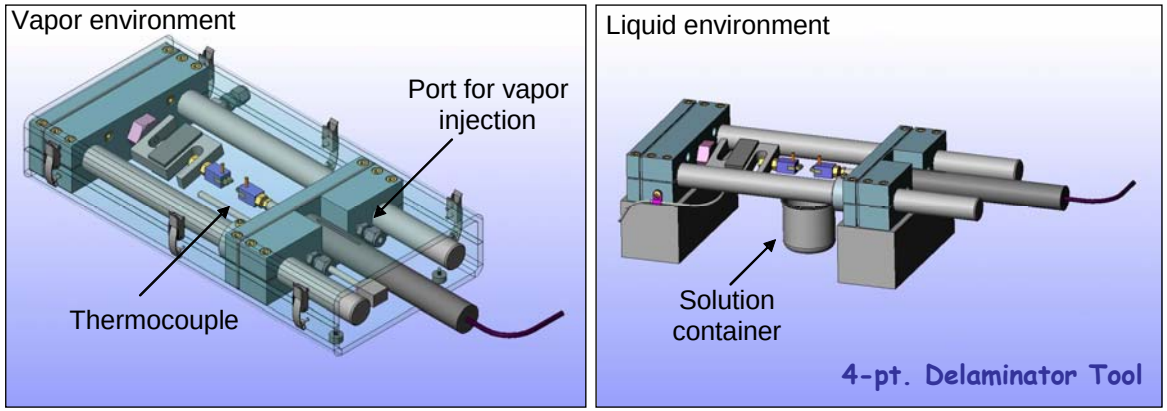
- Control evolution of defects during processing, packaging and service

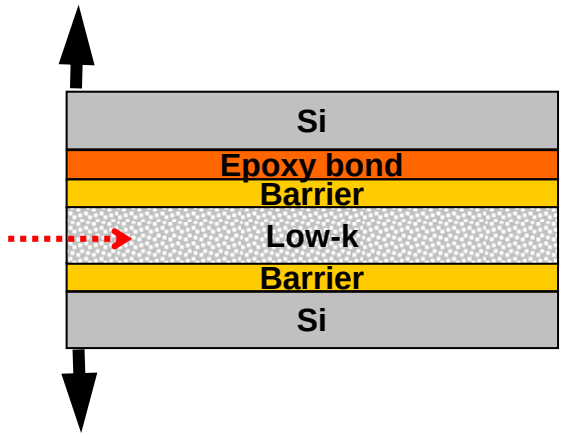




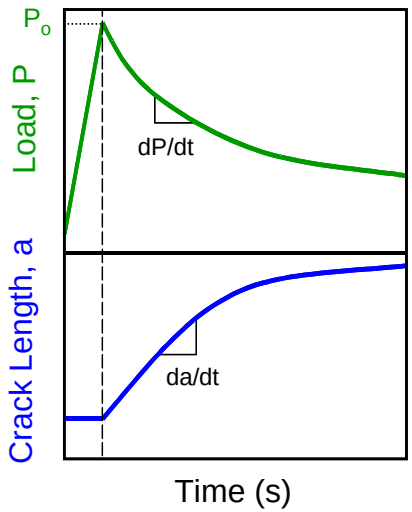
STANFORD MATERIALS SCIENCE AND ENGINEERING

Automated Crack Velocity Testing

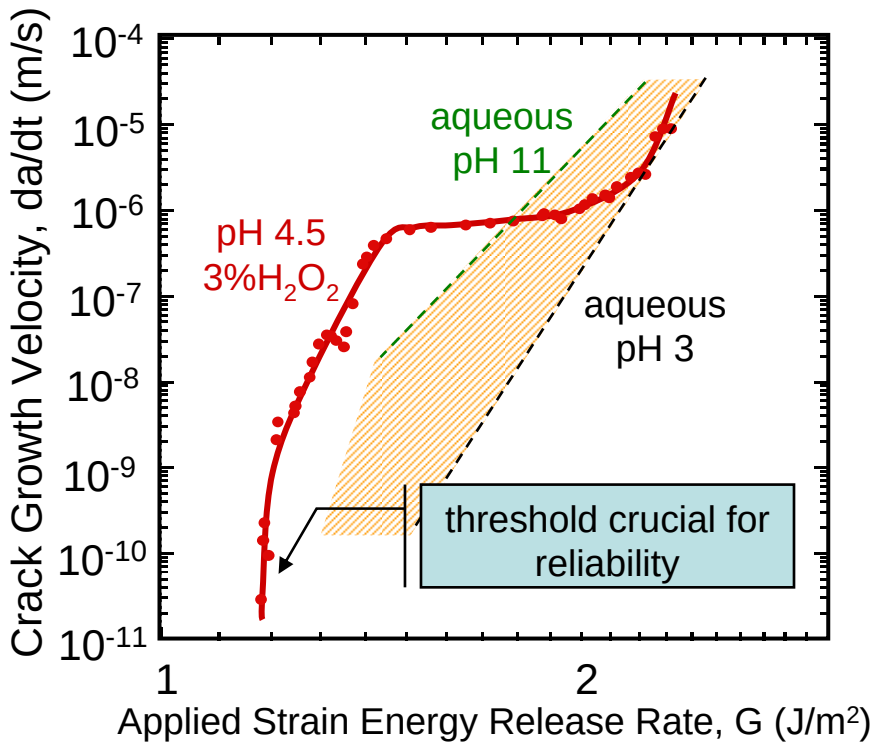




Load Relaxation Crack Growth Technique

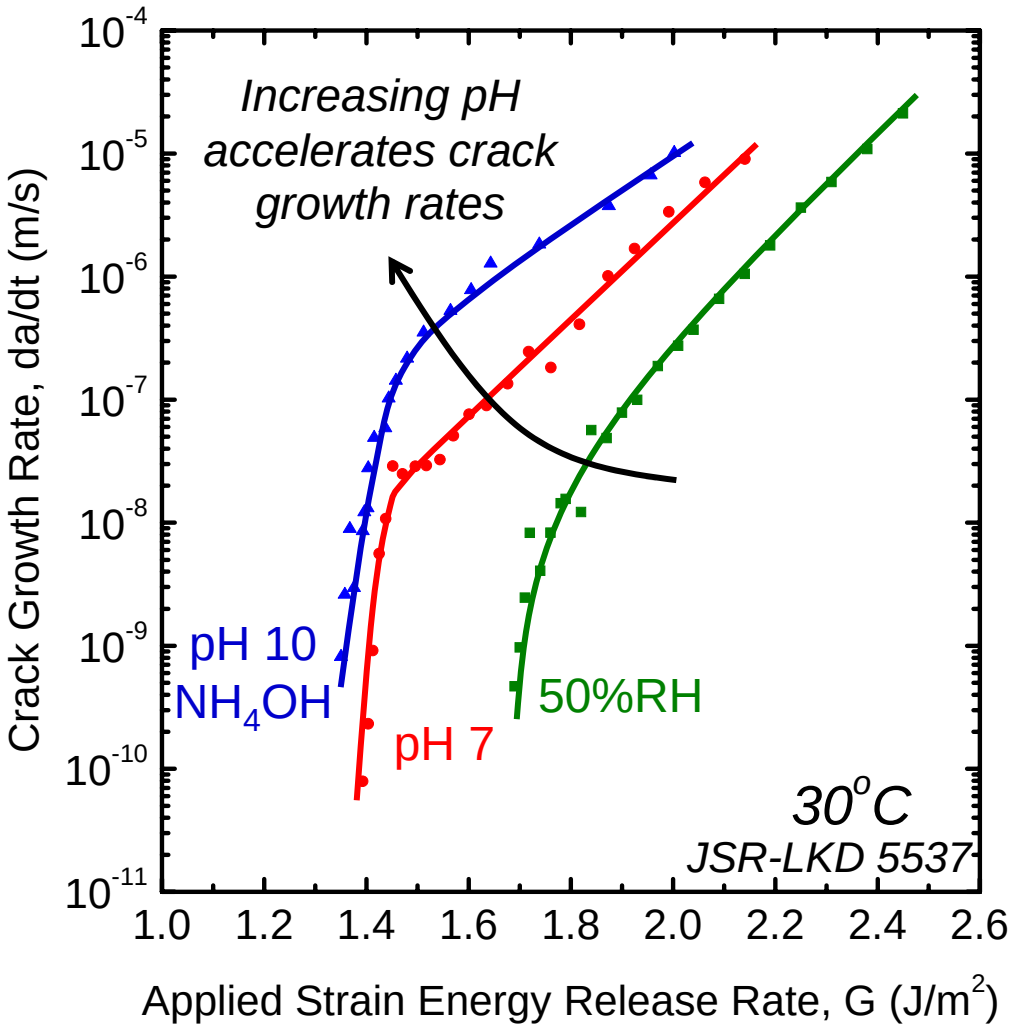


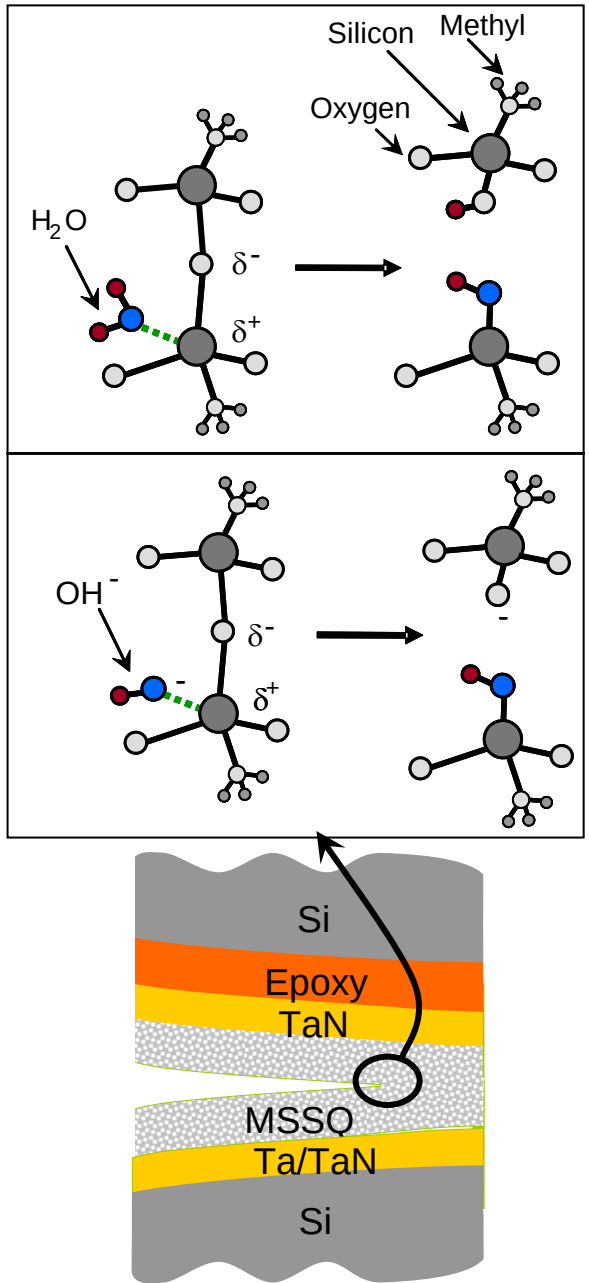
auto analysis



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

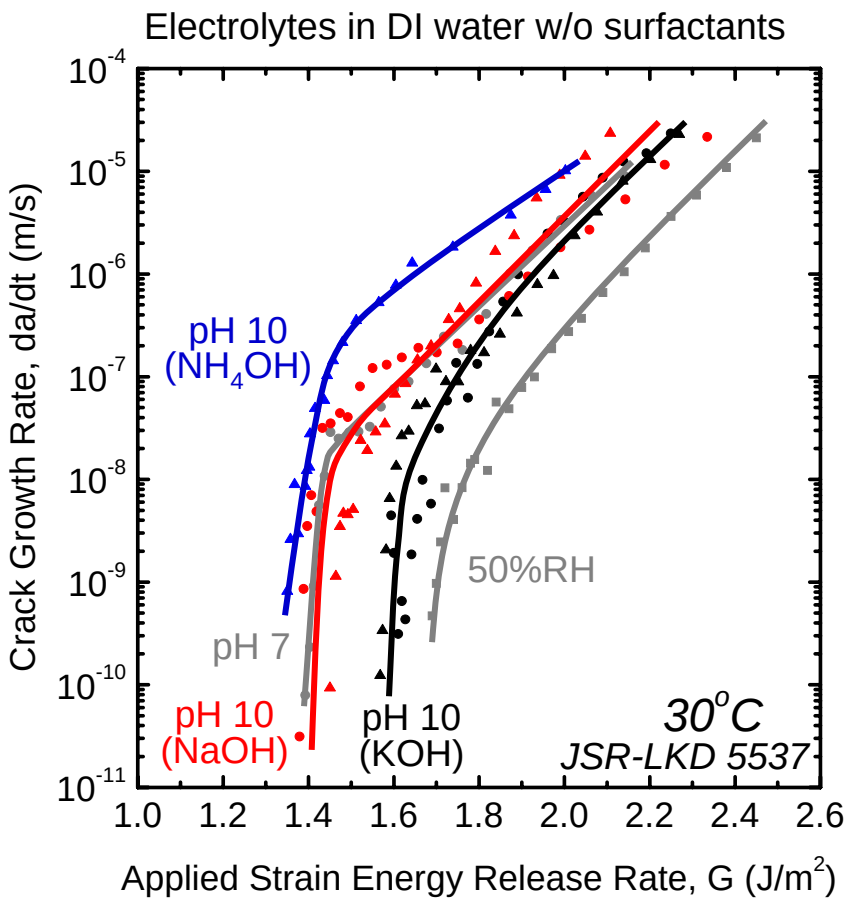
Effects of Solution pH on Crack Growth



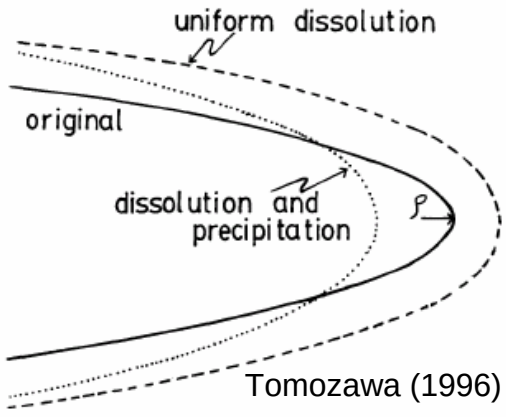


STANFORD
MATERIALS SCIENCE
AND ENGINEERING

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



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

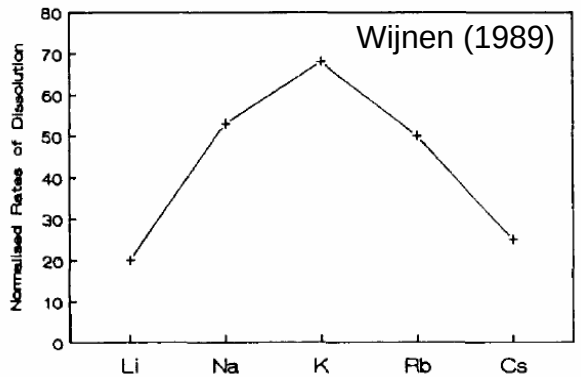


Fig. 5. Normalised rate of dissolution, obtained from ^{29}Si–NMR spectra, as a function of alkali metal hydroxide.

STANFORD MATERIALS SCIENCE AND ENGINEERING

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!

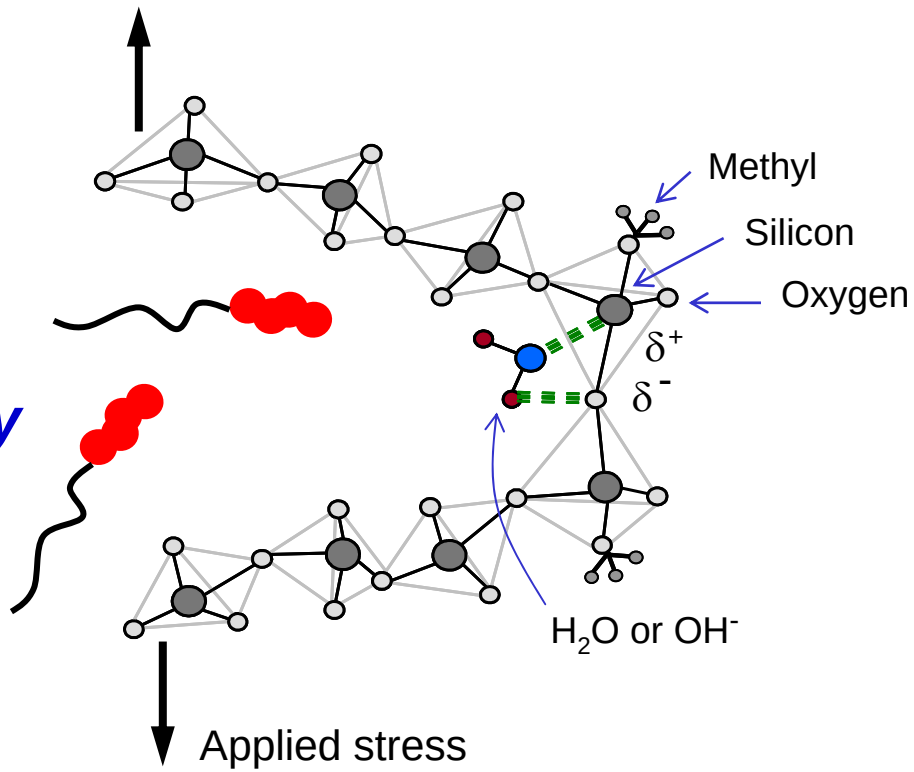
polyoxyethylene alkyl ether

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

Hydrophobic tail | Hydrophilic head

Surfactant molecule

CMP slurry



Nonionic Surfactants: Polyoxyethylene Alkyl Ethers

Monomeric surfactant

$CH_3(CH_2)_{m-1}O(CH_2CH_2O)_nH$ ⇨ 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)

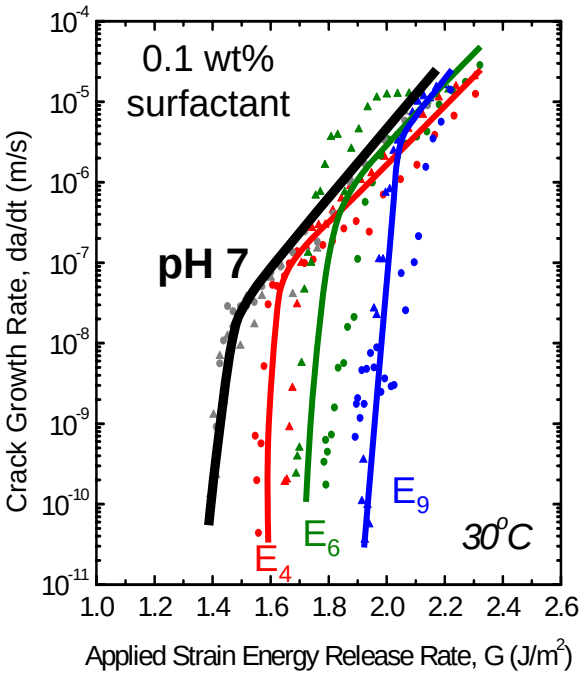
CMC @25 ℃

BRIJ 76: 4×10^{-3} wt%

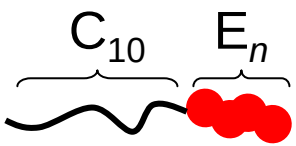
BRIJ 78: 9.5×10^{-4} wt%

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

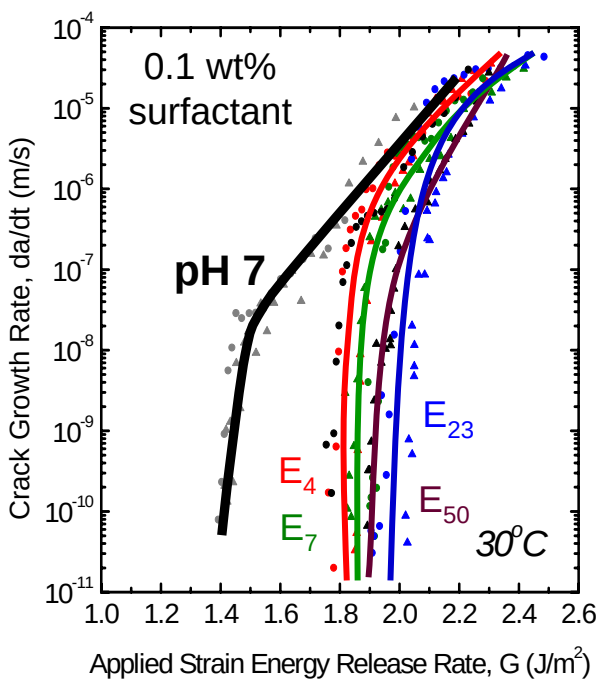
C_{10} E_n



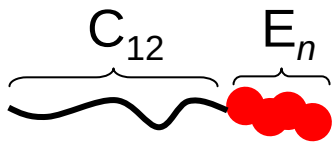
Marked effect on crack growth
Sensitive to hydrophilic chain length



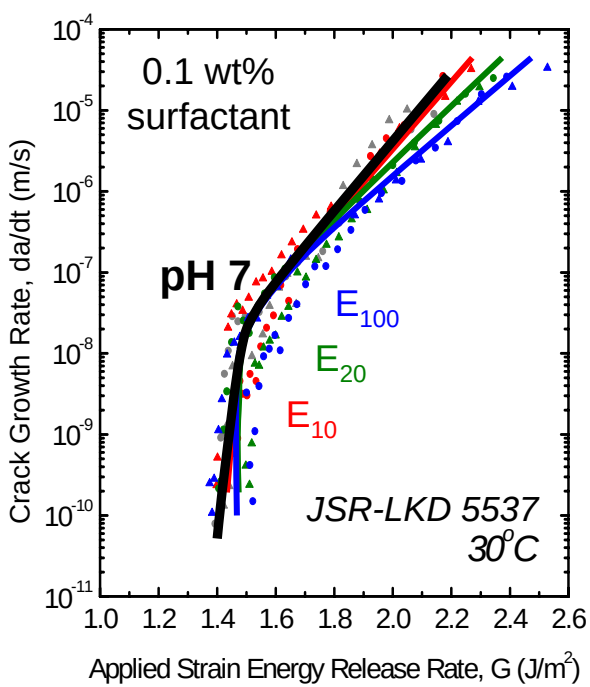
C_{12} E_n



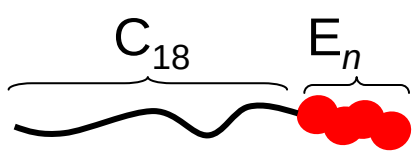
Marked effect on crack growth
Insensitive to hydrophilic chain length



C_{18} E_n



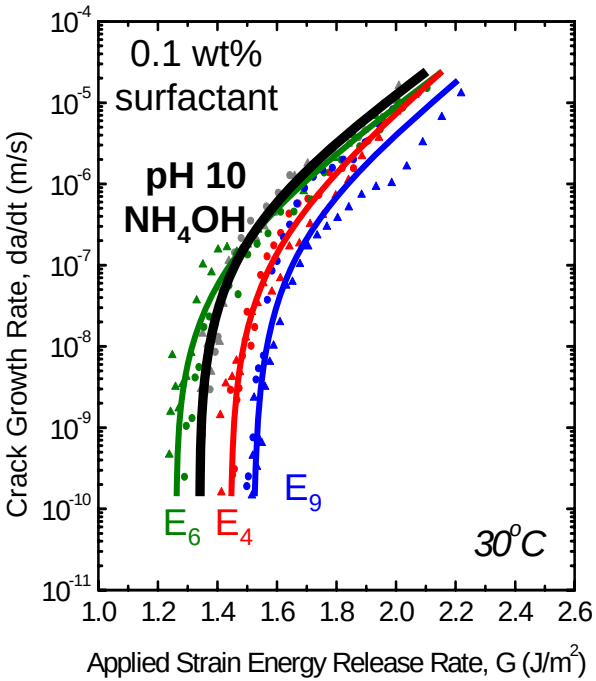
No effect of surfactant molecules



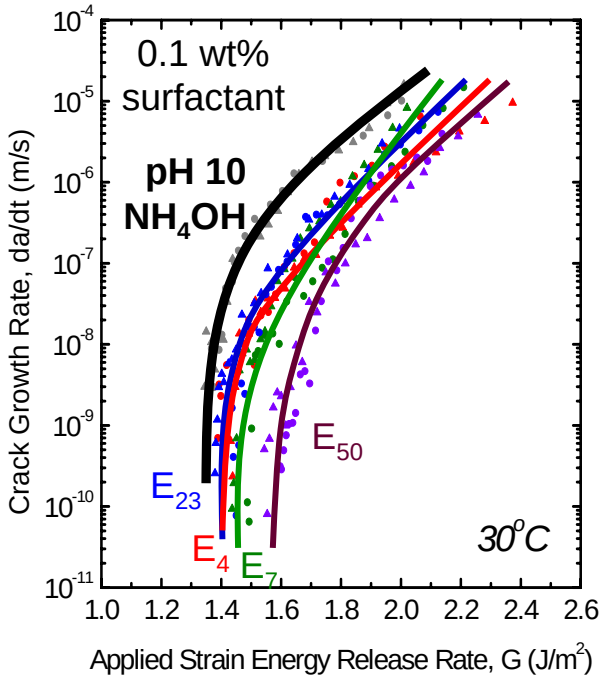
STANFORD
MATERIALS SCIENCE AND ENGINEERING

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

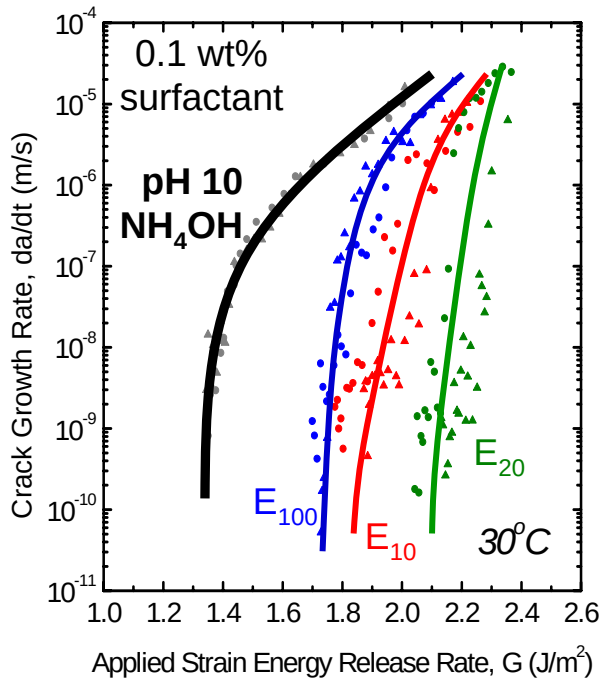
C_{10} E_n



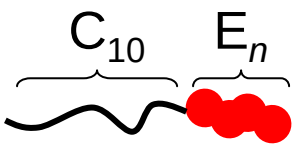
C_{12} E_n



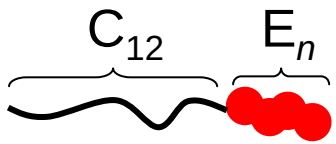
C_{18} E_n



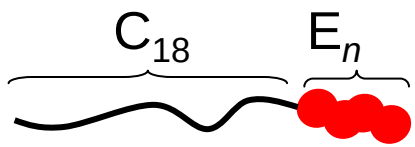
Little effect of surfactant molecules



some effect on crack growth
Insensitive to hydrophilic chain length



Marked effect on crack growth
Sensitive to hydrophilic chain length

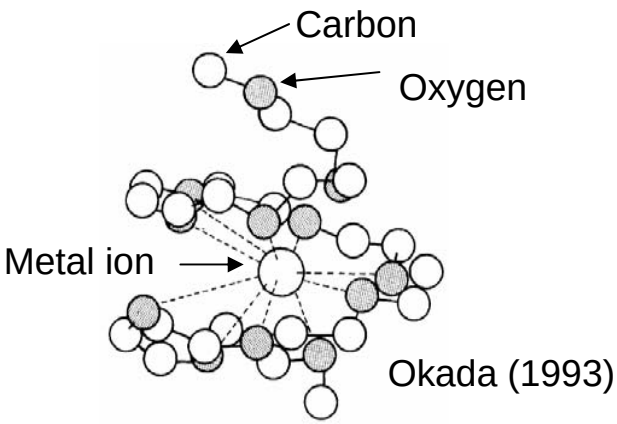


STANFORD
MATERIALS SCIENCE
AND ENGINEERING

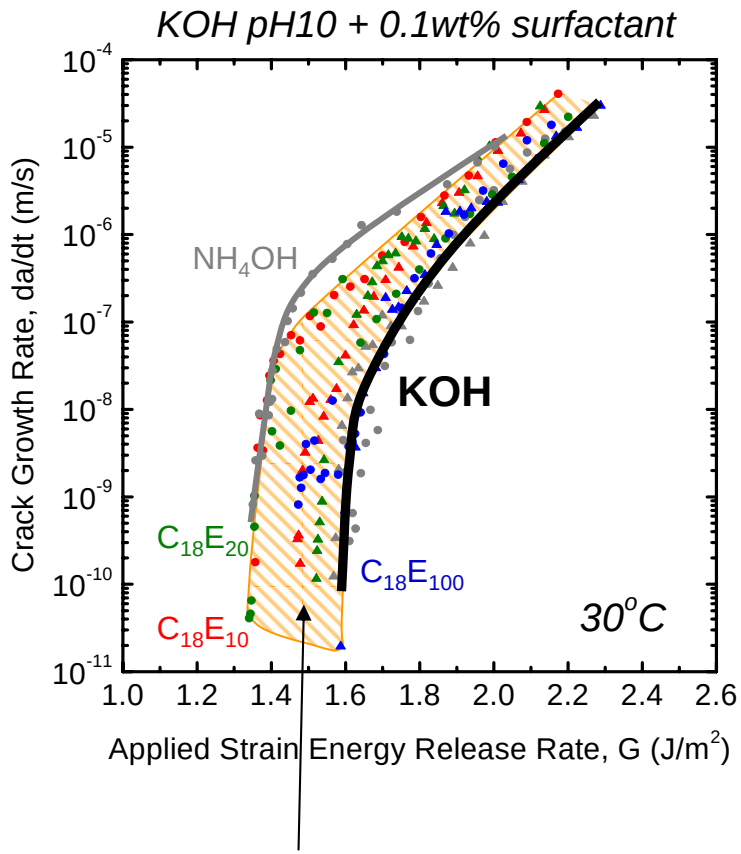
C_mE_n Effects on Crack Growth Behavior (in pH 10 KOH)

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

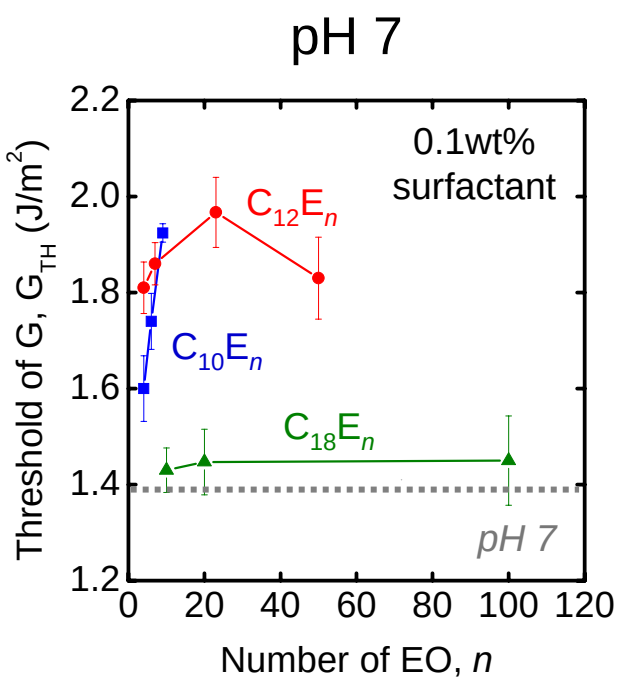


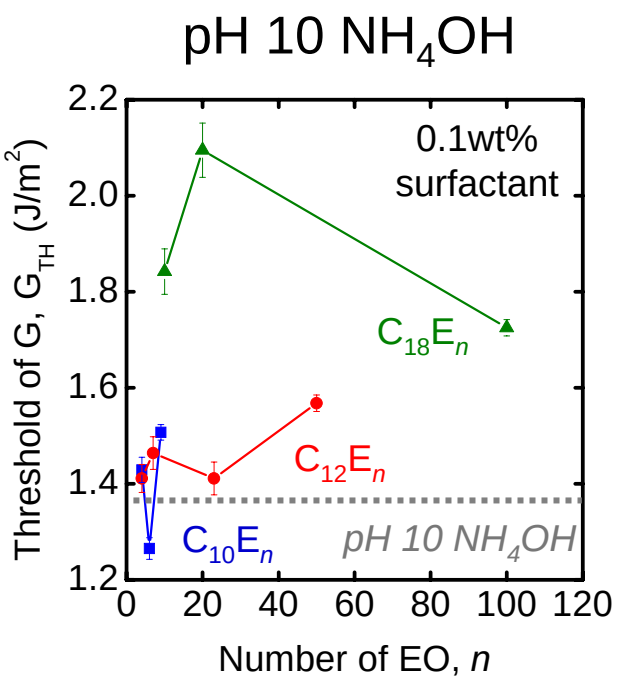
Crack tip blunting effects suppressed by shielding of potassium ion.

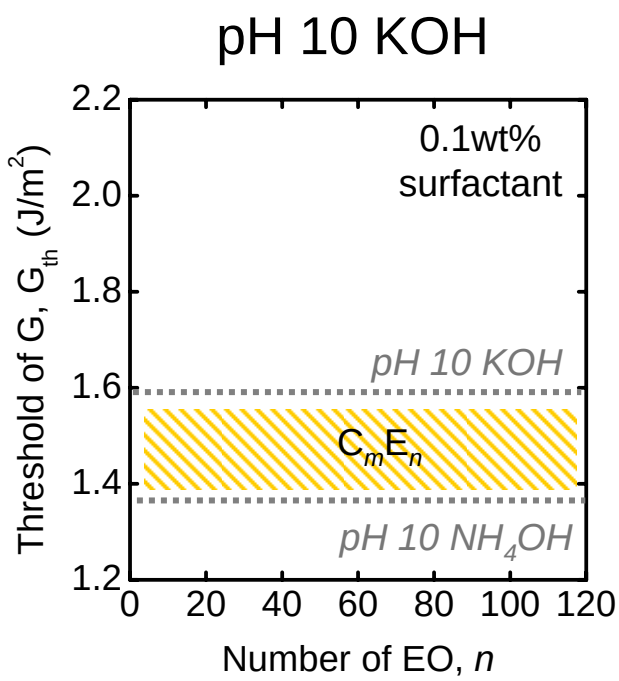
Also, complexation reduces hydrogen bonding sites ↓→ $G_{bridging}$ ↓

STANFORD MATERIALS SCIENCE AND ENGINEERING

Threshold Applied Strain Release Rate (C_mE_n)



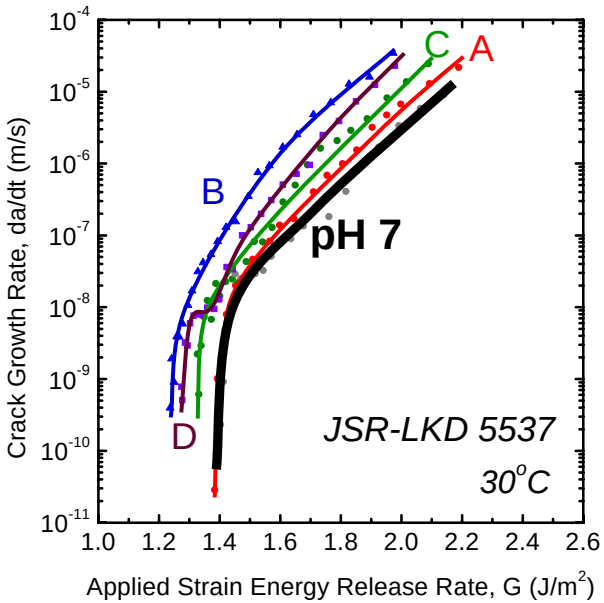




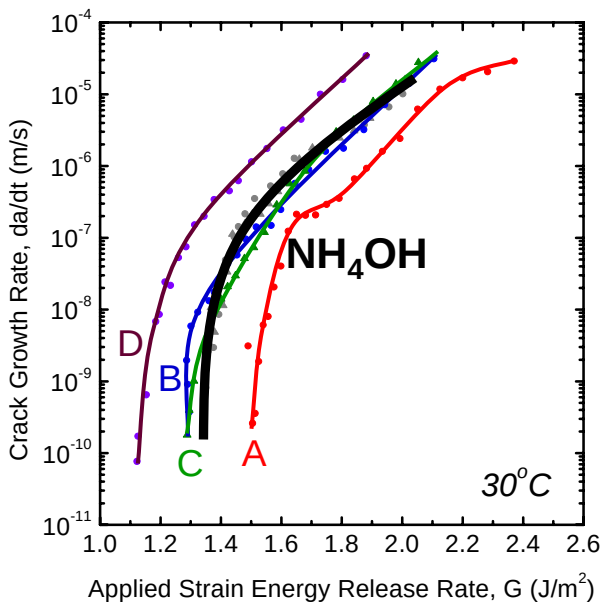
STANFORD
MATERIALS SCIENCE
AND ENGINEERING

Nonionic Gemini (Dimeric) Surfactants Effects on Crack Growth Behavior

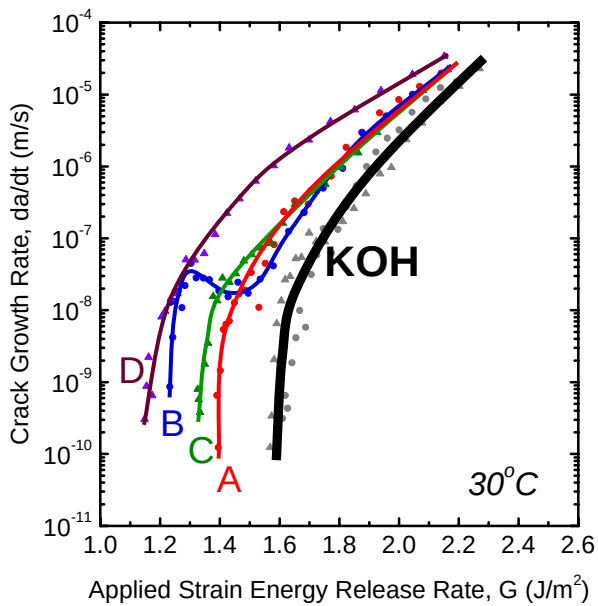
pH 7 + 0.1wt% surfactant



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

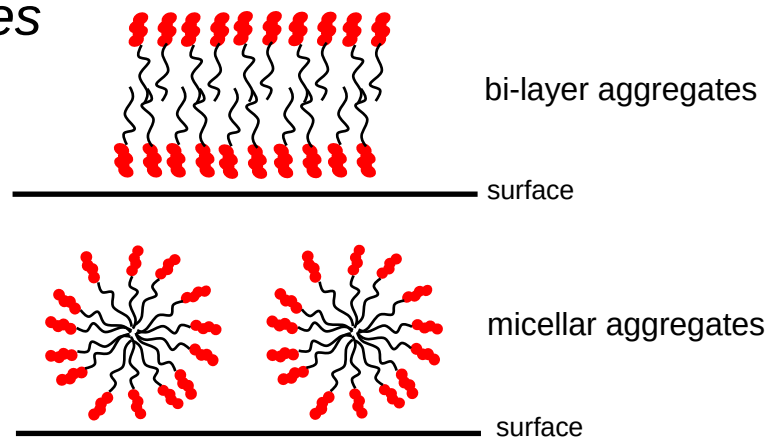
organization into aggregates depends on molecular type, concentration, temperature, pH, ionic content, surfaces, confinement….

- C_mE_n

small n (large m) — *high*

large n (small m) — *low*

- *SiO_2 surface binding sites*



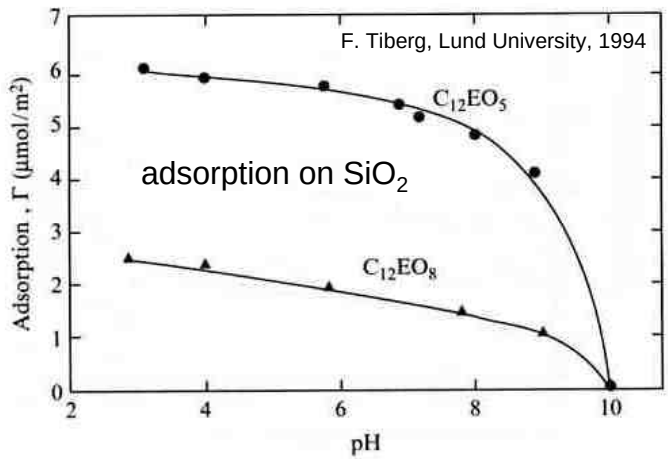
- *confinement in cracks or pores*

1-D surface / surface, δ — crack surfaces

2-D — cylindrical pores

3-D — pores

- *pH effects*



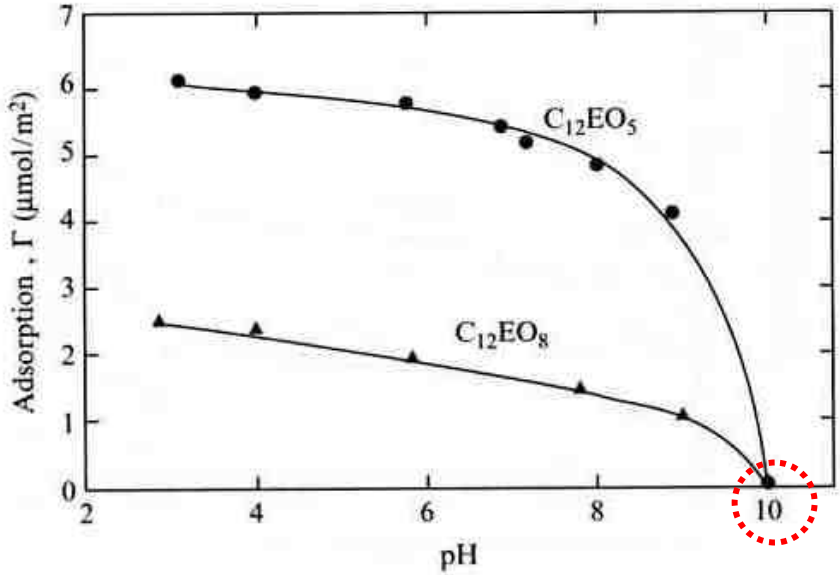
STANFORD MATERIALS SCIENCE AND ENGINEERING

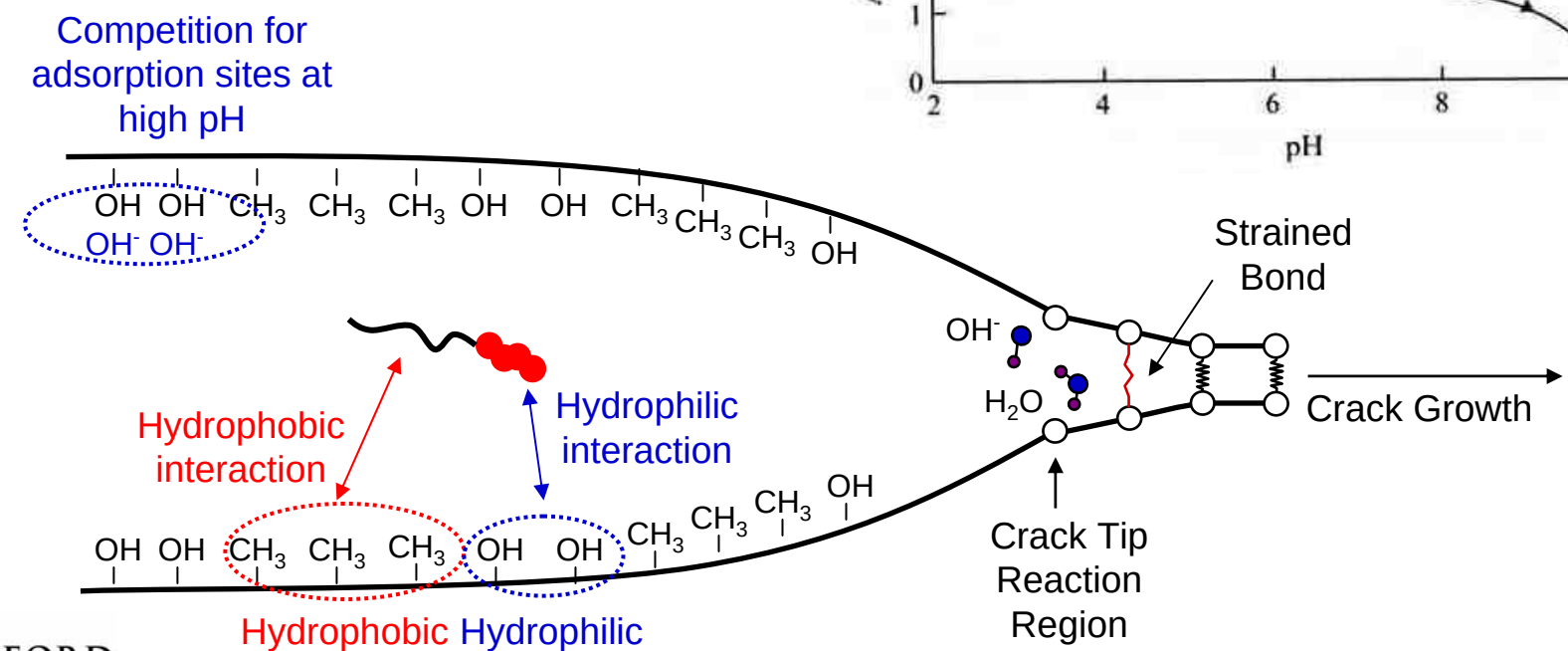
Hydrophobic and Hydrophilic Interactions

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].

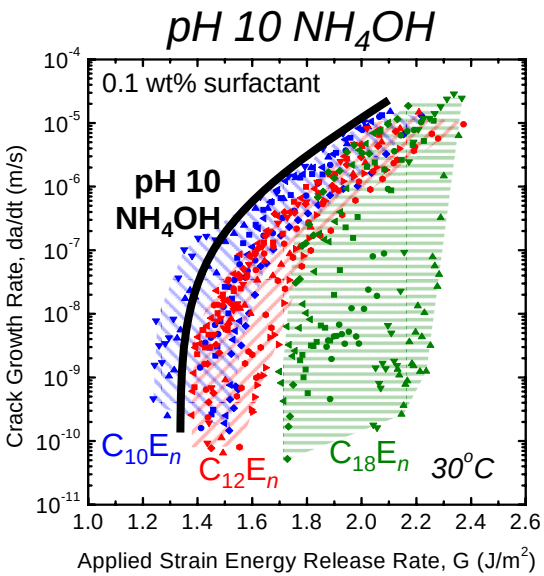
Adsorption on the silica surface

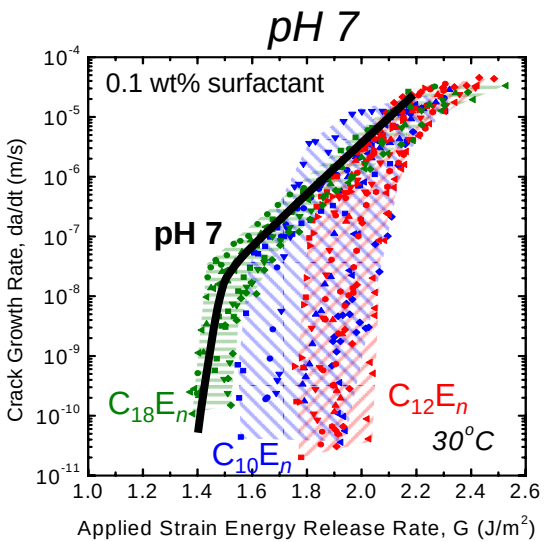




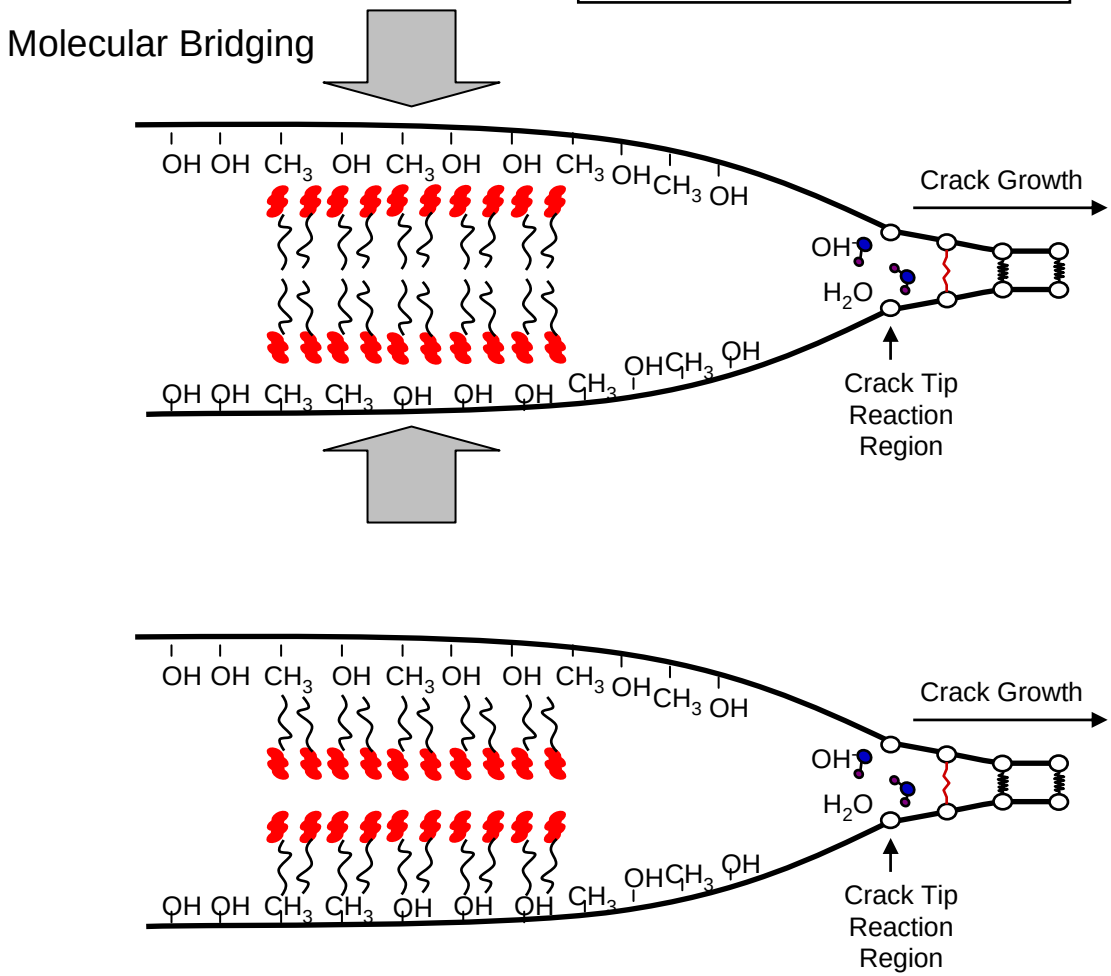
STANFORD MATERIALS SCIENCE AND ENGINEERING

Molecular Bridging in Aqueous Solution

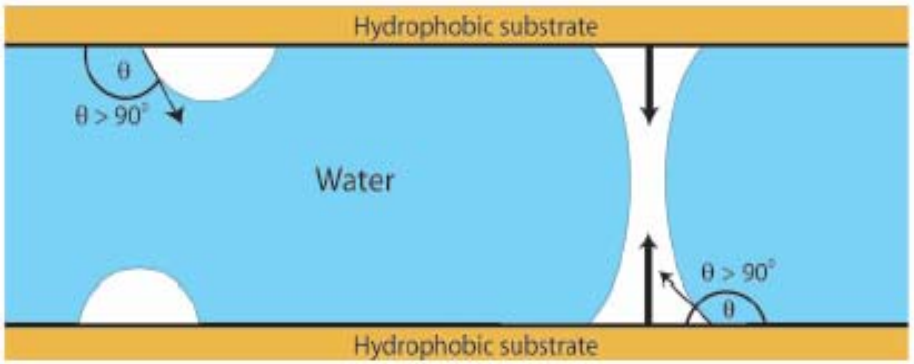




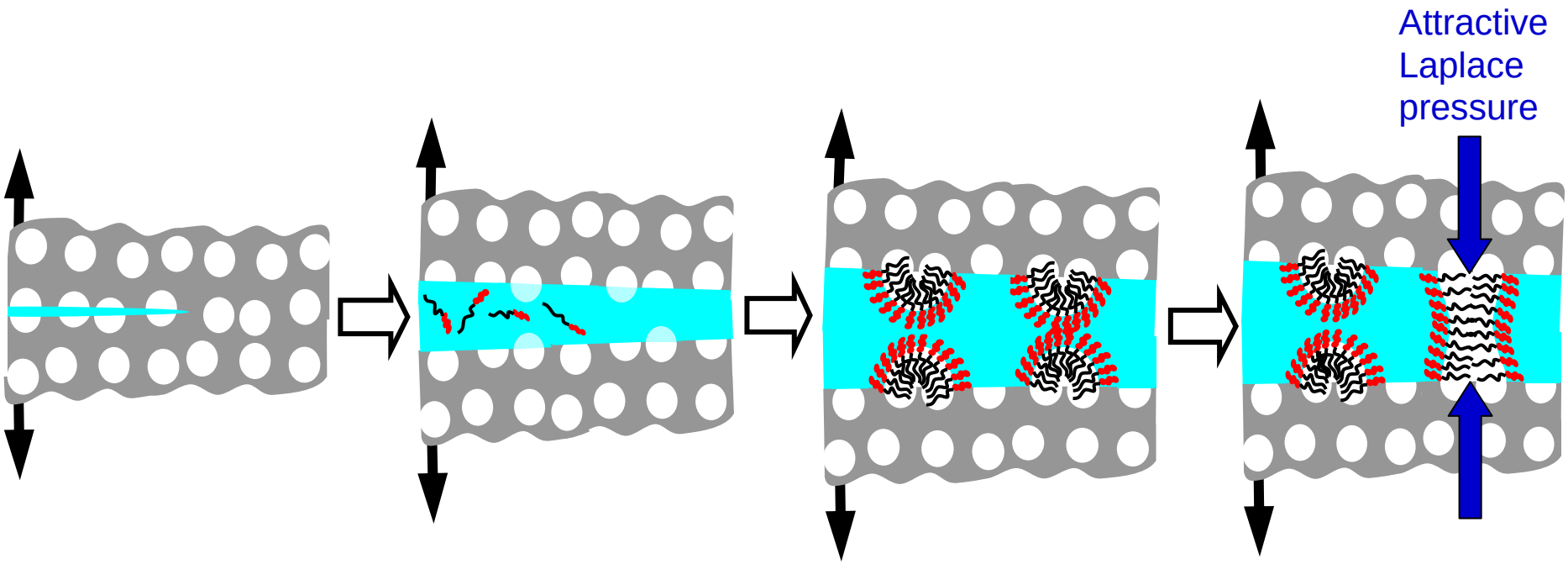
$$G_{tip} = G_{applied} - G_{bridging}$$



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]

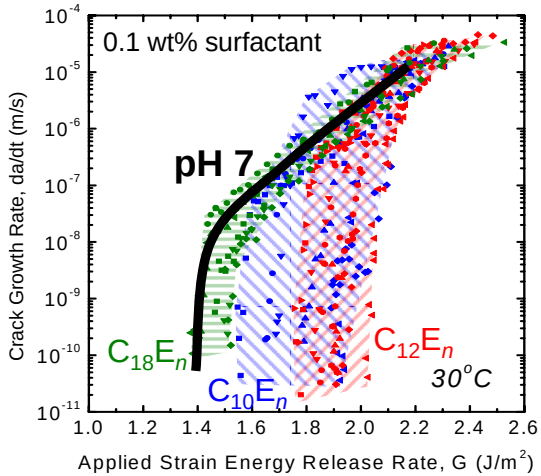


Conclusions

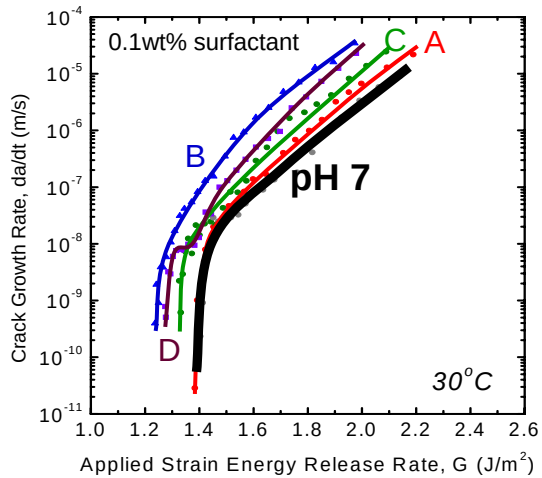
Effects of surfactant additions on the defect evolution

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.

STANFORD MATERIALS SCIENCE AND ENGINEERING

JSR Micro JSR MATERIALS INNOVATION

Q & A