Role of Stress and Solution Chemistry for Reduced Damage During CMP of Ultra-Low-k Materials

July 17, 2007

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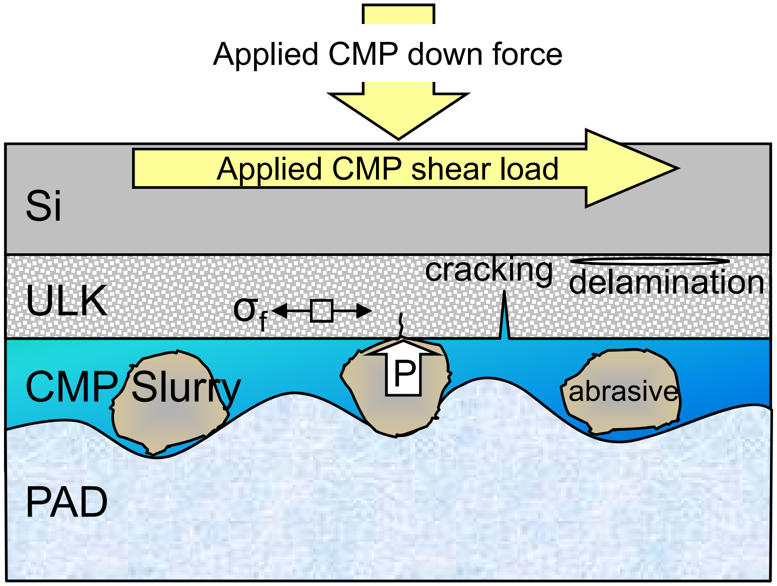
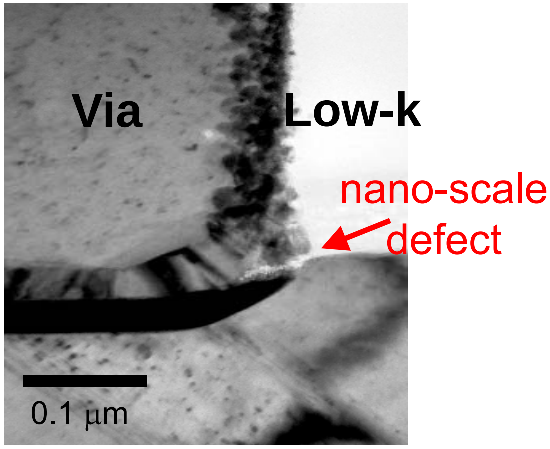
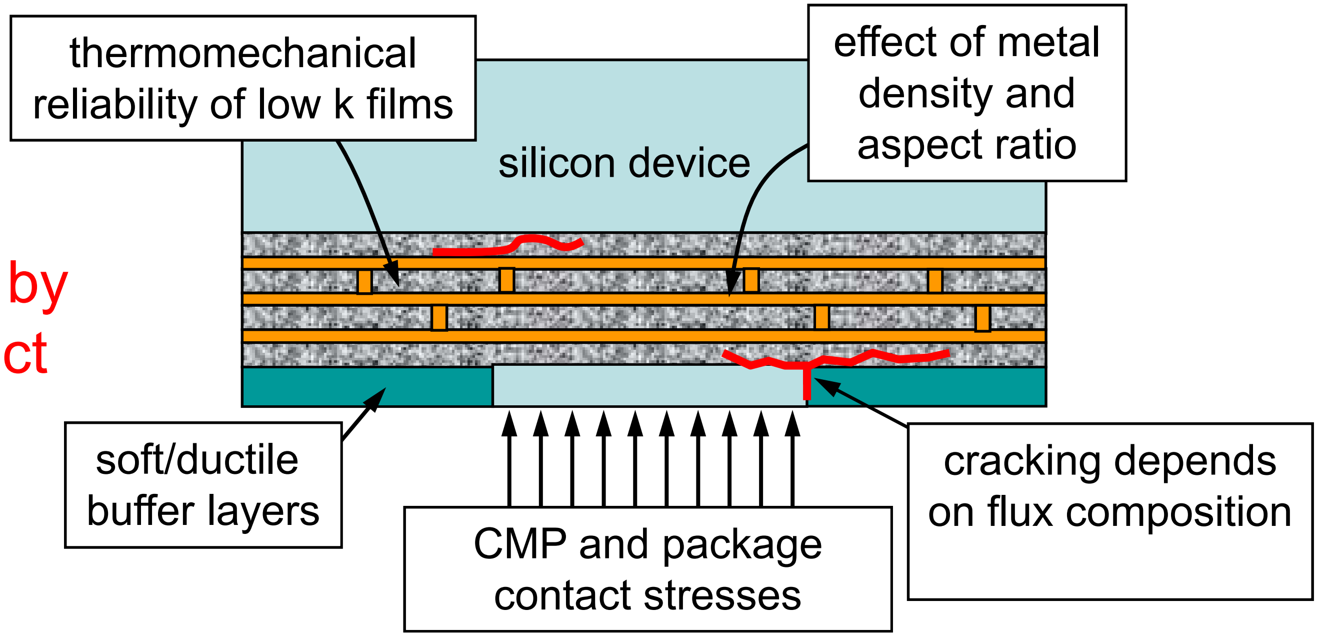
Reliable Processing of Interconnect Structures





Process yield and reliability determined by the evolution of defect



thermomechanical reliability of low k films

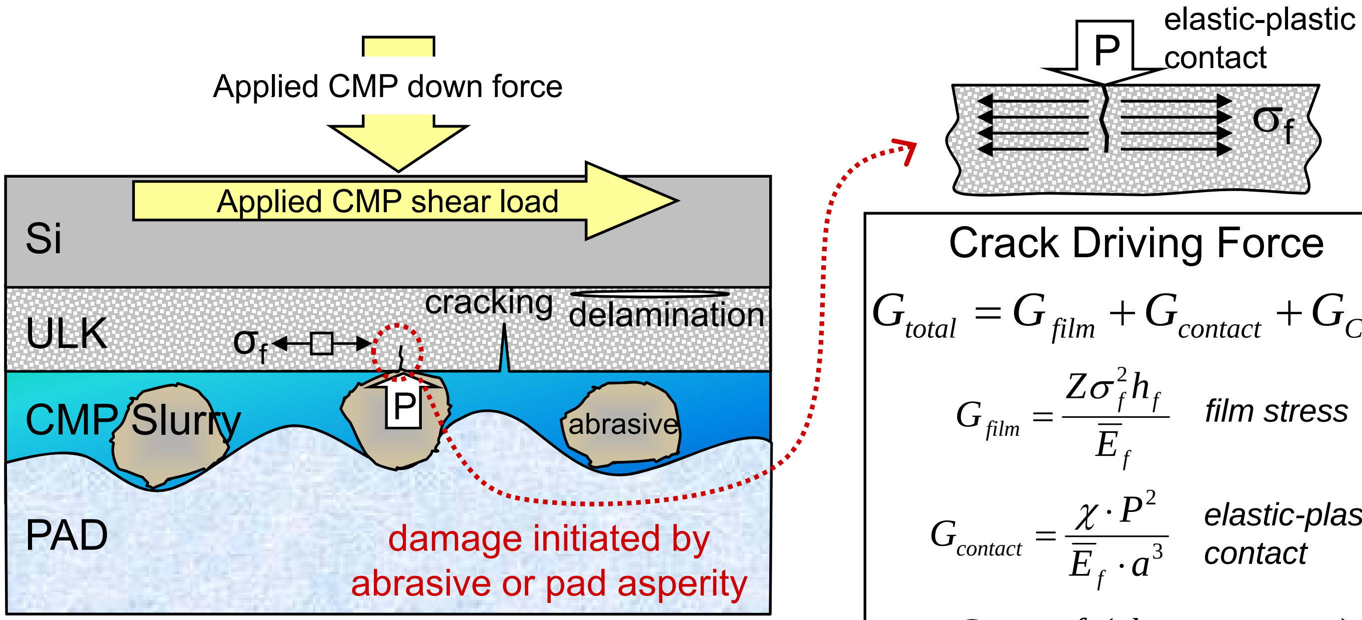
effect of metal density and aspect ratio

soft/ductile buffer layers

CMP and package contact stresses

cracking depends on flux composition

Crack Driving Force



Crack Driving Force

$$G_{total} = G_{film} + G_{contact} + G_{CMP}$$

$$G_{film} = \frac{Z\sigma_f^2 h_f}{\bar{E}_f}$$ *film stress*

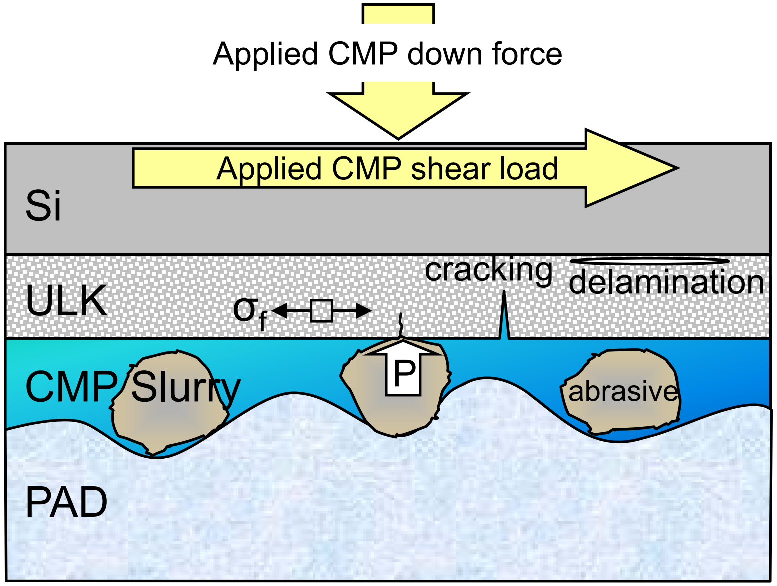
$$G_{contact} = \frac{\chi \cdot P^2}{\bar{E}_f \cdot a^3}$$ *elastic-plastic contact*

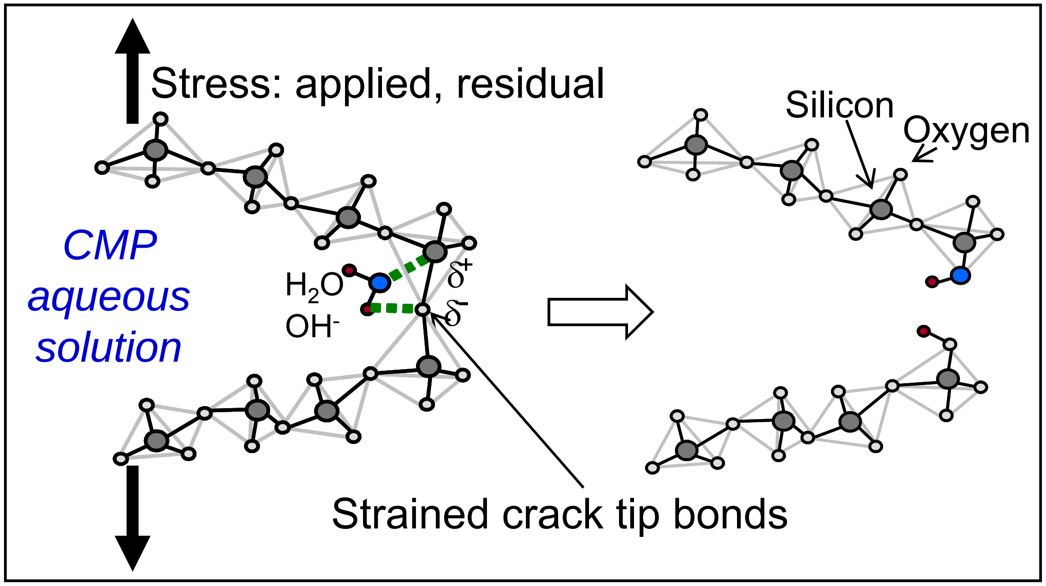
$$G_{CMP} = fn(shear, pressure)$$

In the absence of chemically active environmental species, crack propagates if

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

Environment-Assisted Cracking





$$Si-O-Si + H_2O \xrightarrow{stress} Si-OH + Si-OH$$

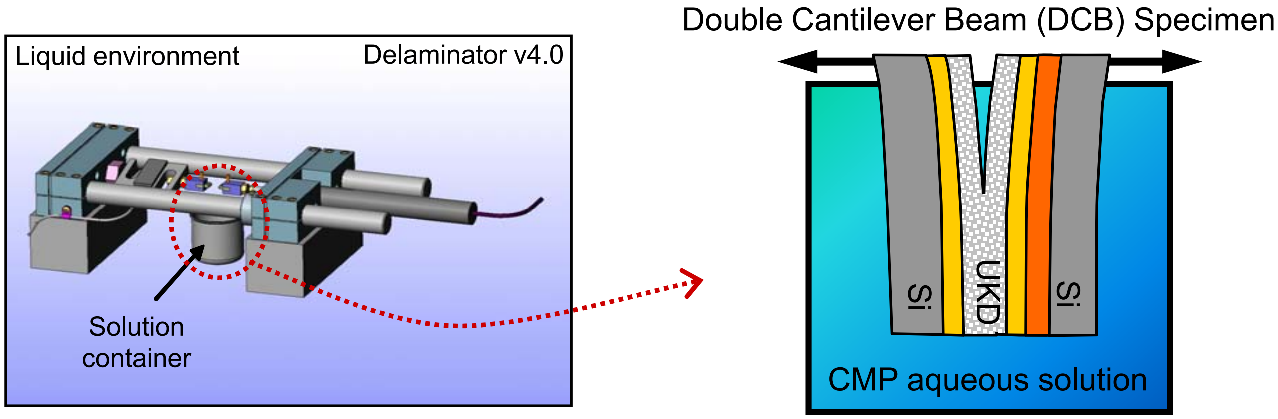
$$Si-O-Si + OH^- \xrightarrow{stress} Si-OH + Si-O^-$$

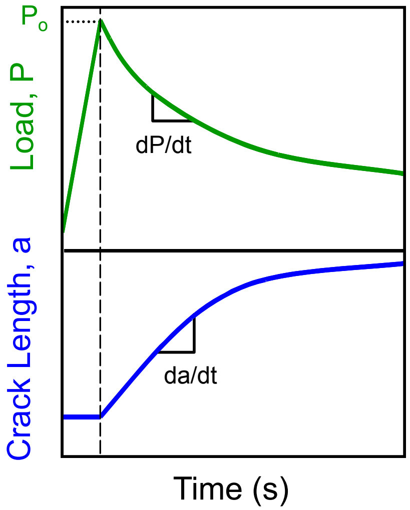
In the presence of chemically active species, crack propagates even if

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

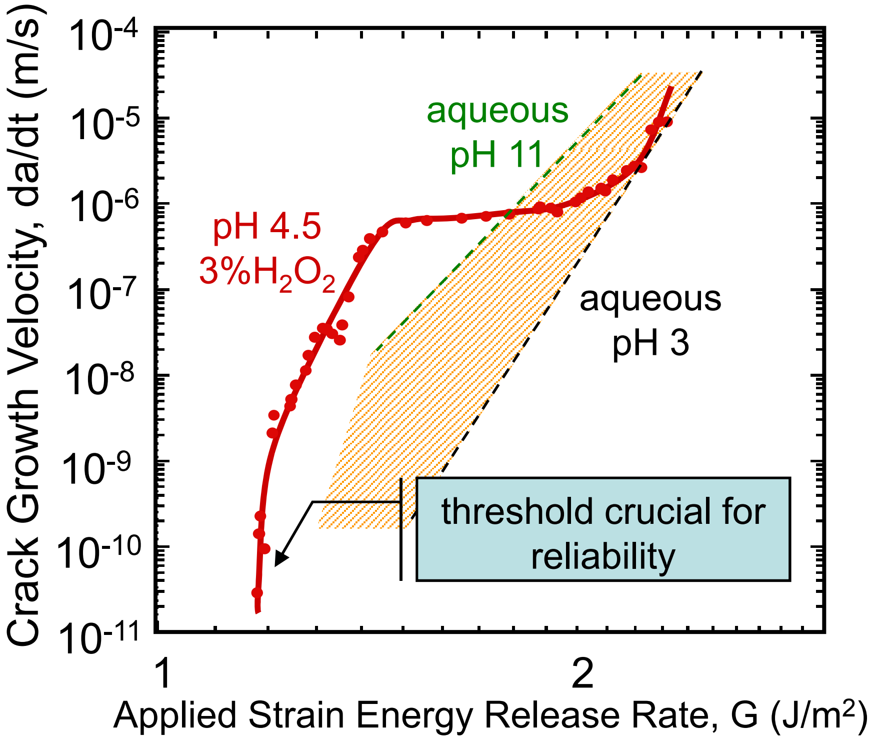
Kinetic fracture

Load Relaxation Crack Growth Technique





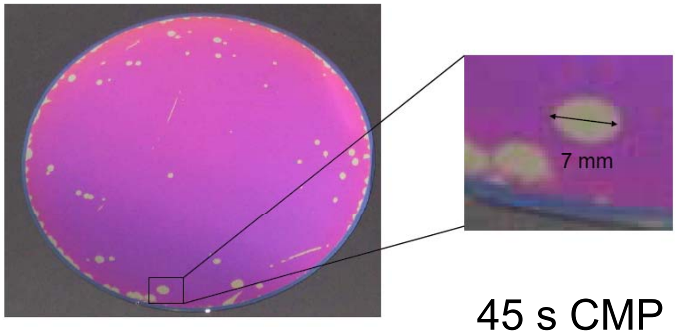
auto analysis



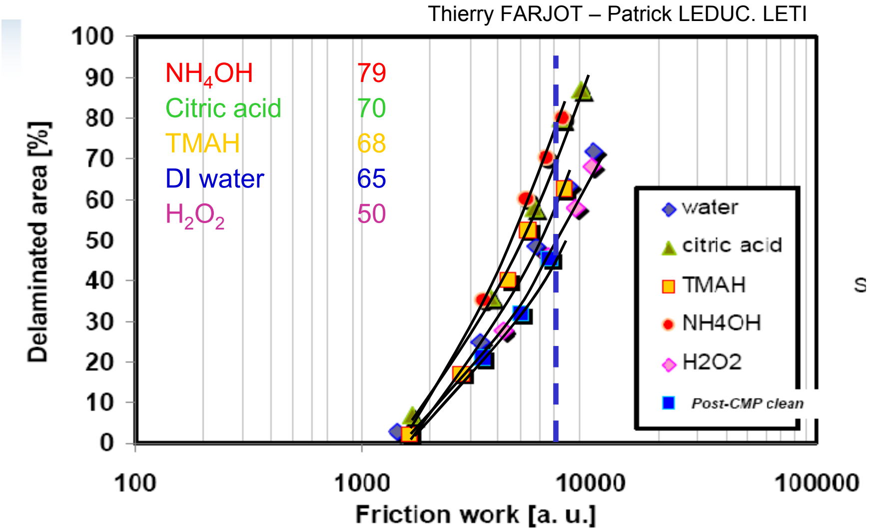
threshold crucial for reliability

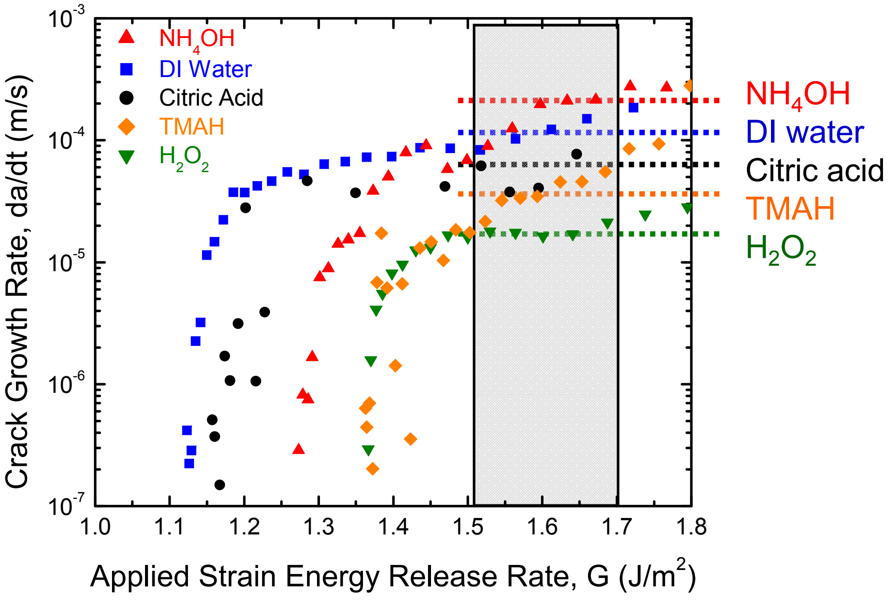
System and support:
DTS Company, Menlo Park, CA (dauskardt@stanford.edu)

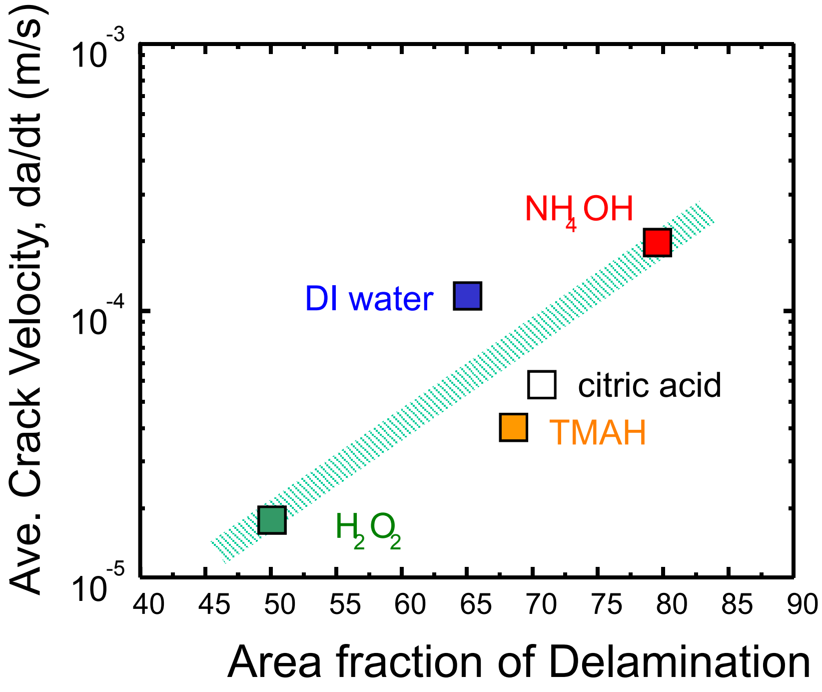
Relevance to CMP Damage



45 s CMP

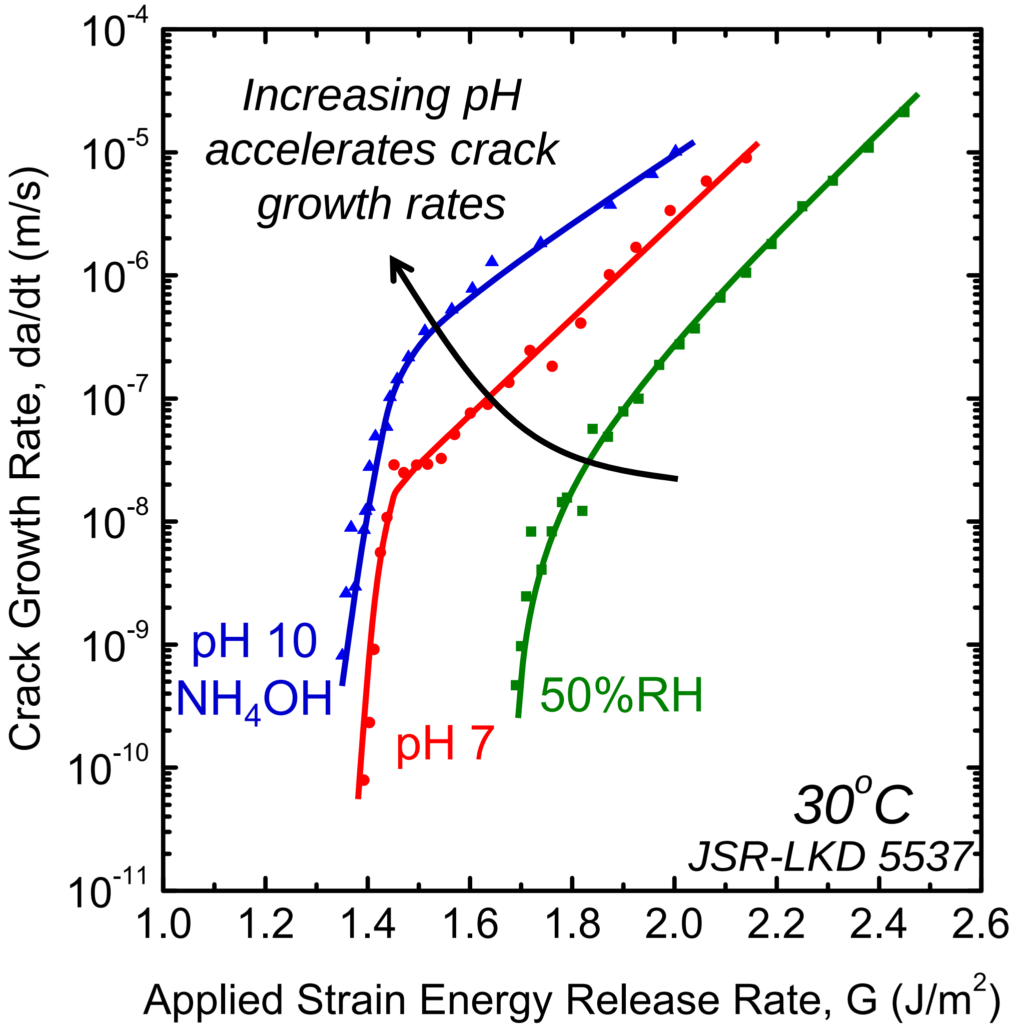


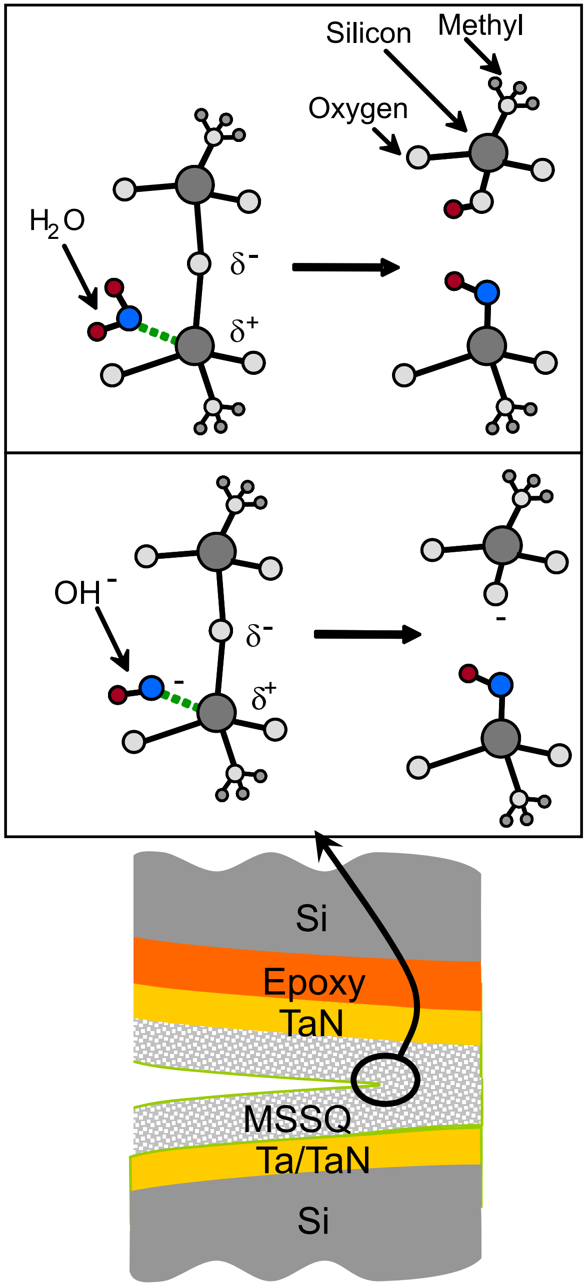




Courtesy of Markus D. Ong and Reinhold H. Dauskardt, MRS Spring Meeting, 2007

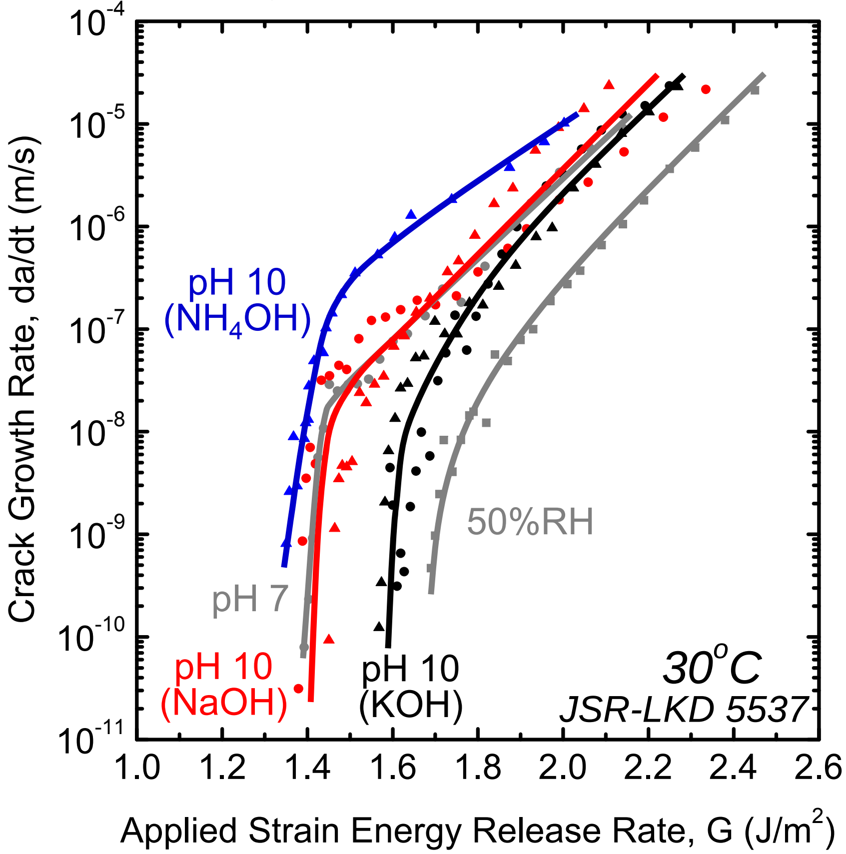
Effects of Solution pH on Crack Growth



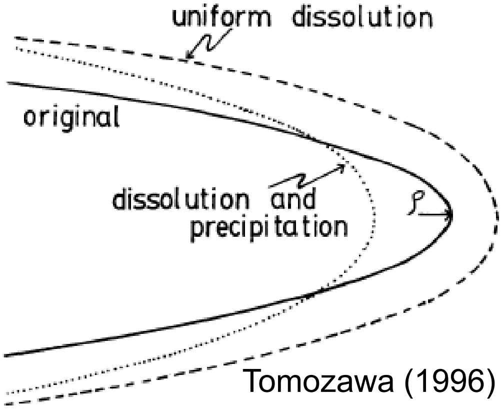


Alkali metal ion + crack tip → decelerated crack growth by crack tip blunting

Electrolytes in DI water w/o surfactants



Crack tip gets blunted by dissolution of the silica backbone.



Tomozawa (1996)

Inglis expression for the stress concentration

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

Silica gel dissolution in aqueous alkali metal hydroxides

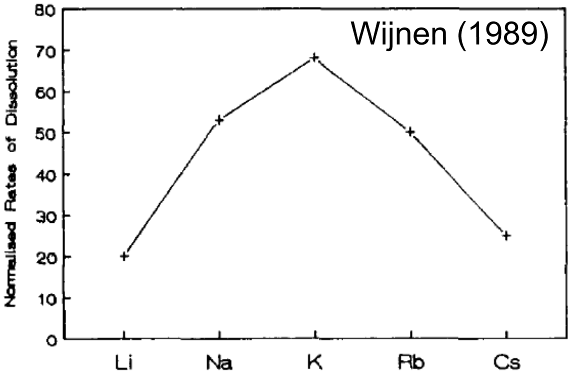


Fig. 5. Normalised rate of dissolution, obtained from ^{29}Si–NMR spectra, as a function of alkali metal hydroxide.

Effects of Nonionic Surfactants on Defect Evolution during CMP

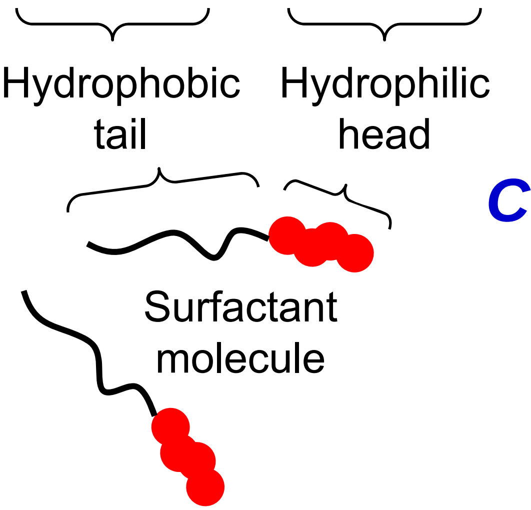
Surfactant additions critical for efficient CMP:

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

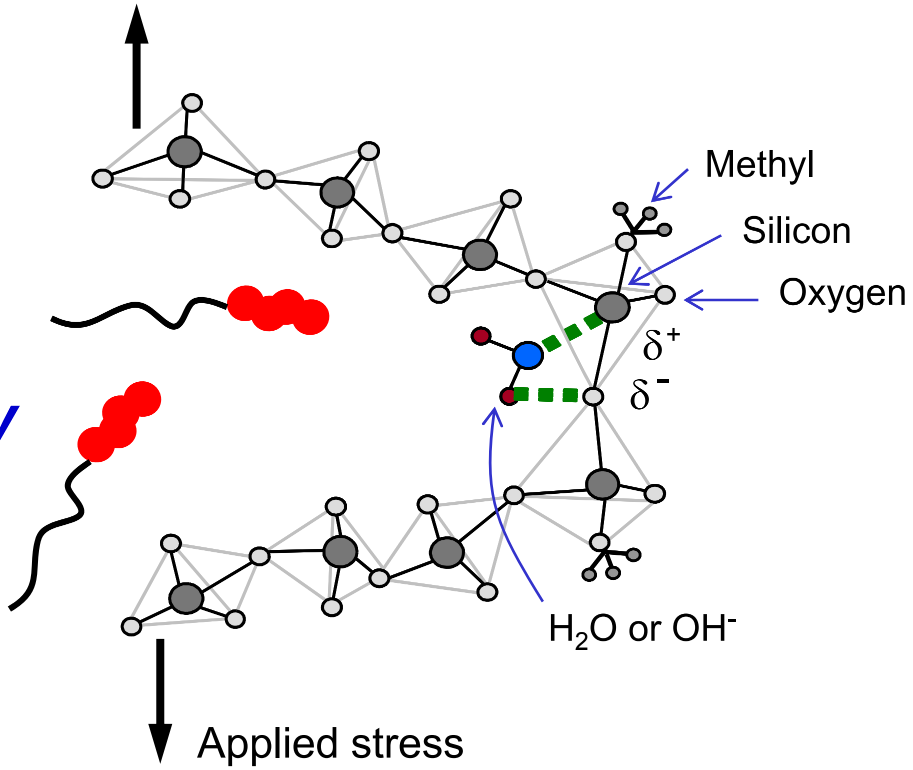
Effects of surfactant molecules on the defect evolution/crack growth are unknown!

polyoxyethylene alkyl ether

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

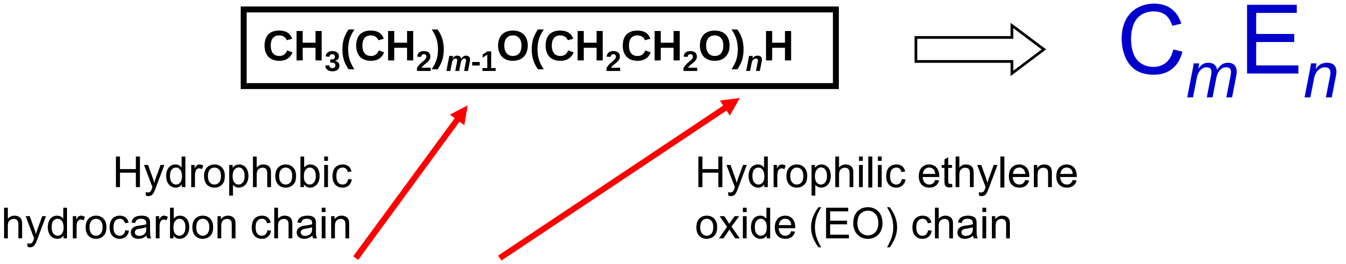


CMP slurry



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)

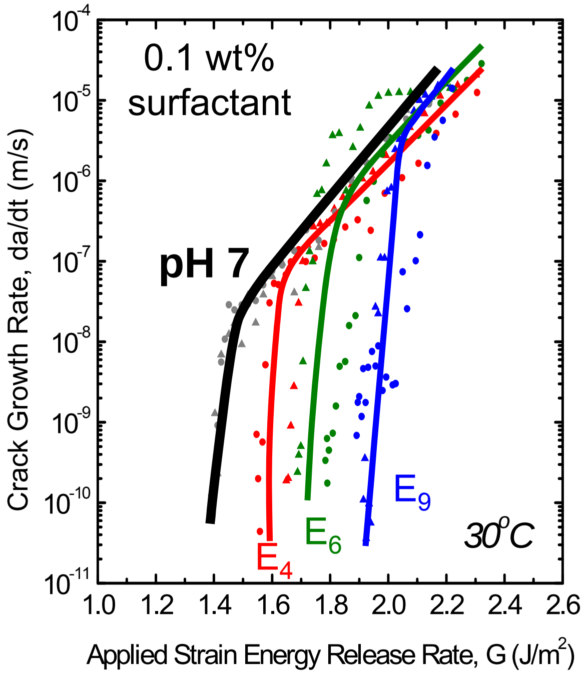
CMC @25°C

BRIJ 76: $4\text{x}10^{-3}$ wt%

BRIJ 78: $9.5\text{x}10^{-4}$ wt%

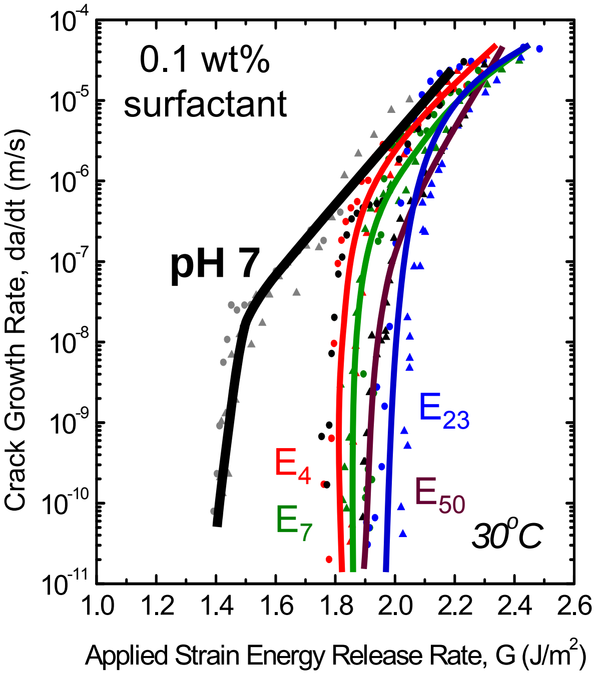
C_mE_n Effects on Crack Growth Behavior (in pH 7 NH_4OH)

C_{10} E_n



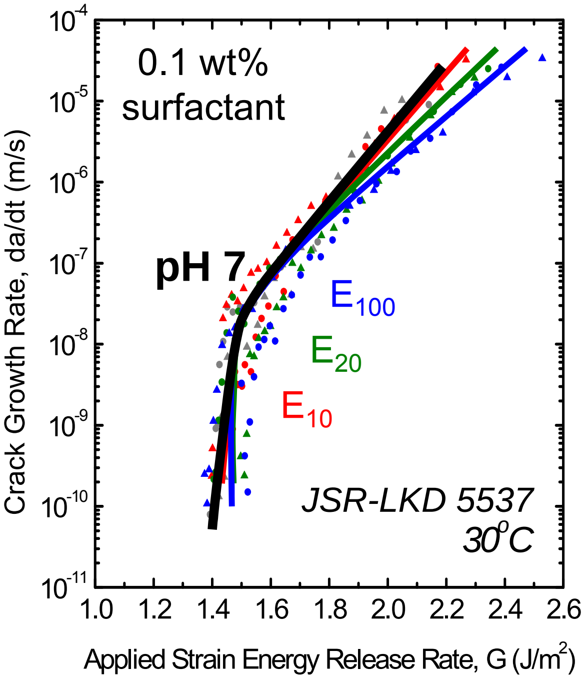
Marked effect on crack growth
Sensitive to hydrophilic chain length

C_{12} E_n

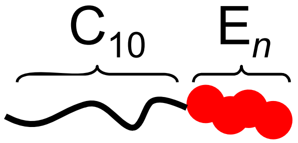


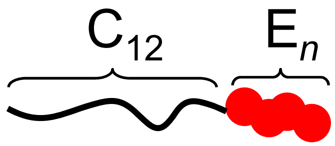
Marked effect on crack growth
Insensitive to hydrophilic chain length

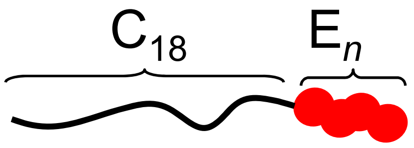
C_{18} E_n



No effect of surfactant molecules

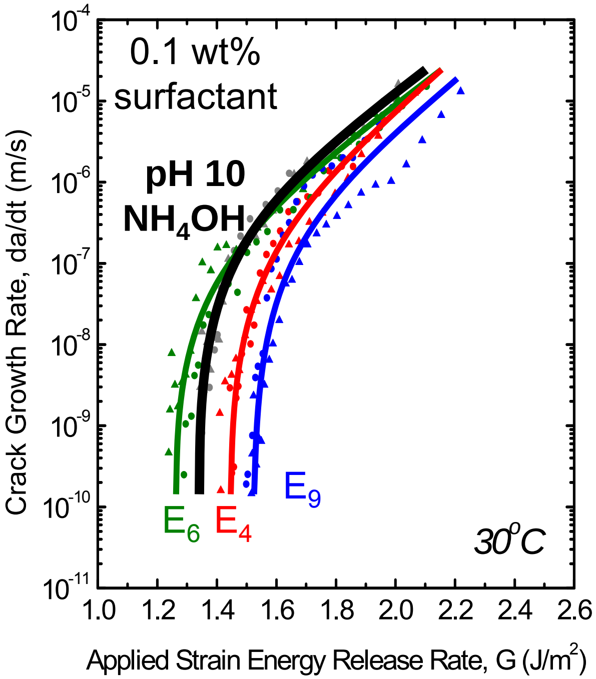




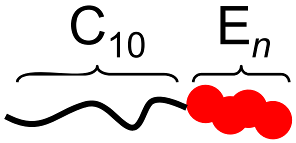


C_mE_n Effects on Crack Growth Behavior (in pH 10 NH_4OH)

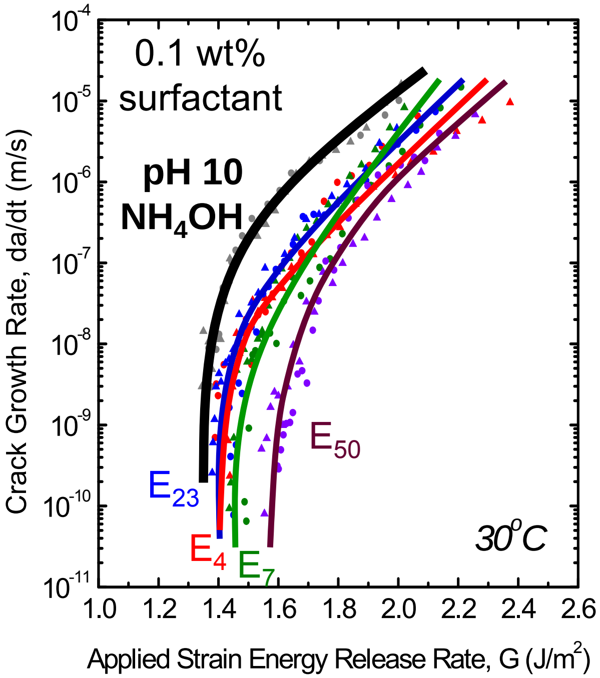
C_{10} E_n



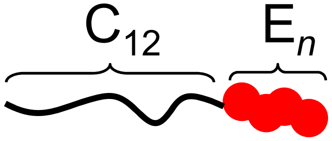
Little effect of surfactant molecules



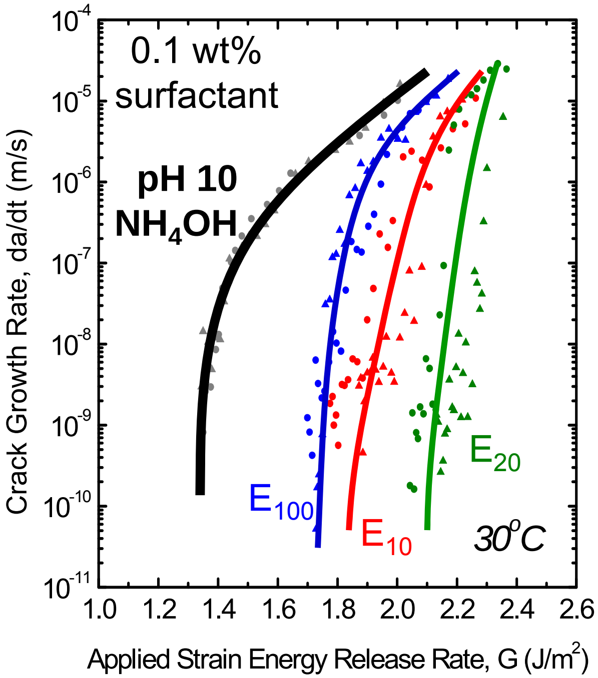
C_{12} E_n



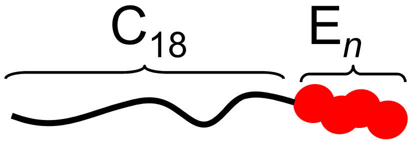
some effect on crack growth
Insensitive to hydrophilic chain length



C_{18} E_n



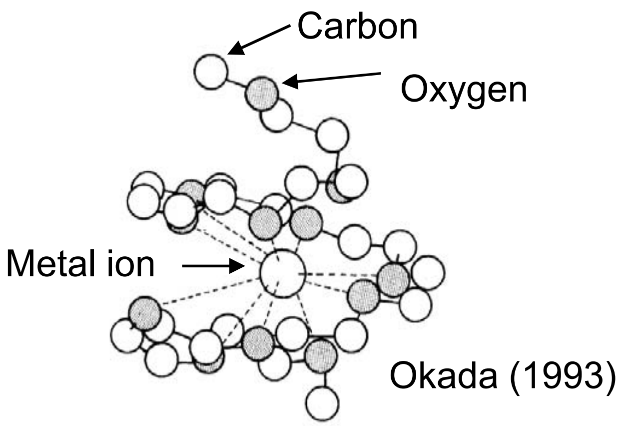
Marked effect on crack growth
Sensitive to hydrophilic chain length



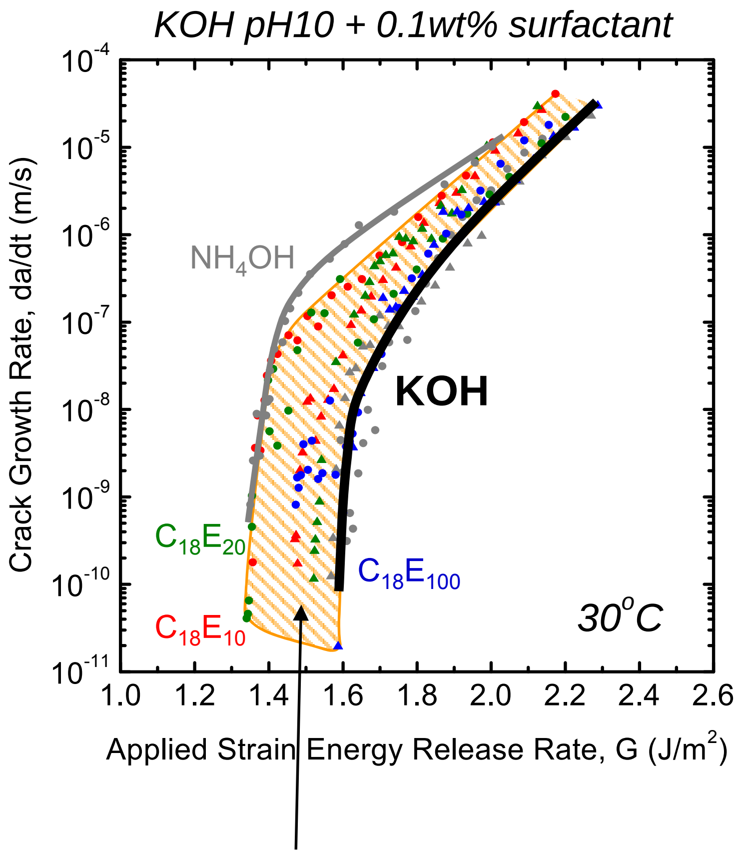
C_mE_n Effects on Crack Growth Behavior (in pH 10 KOH)

Alkali metal ion + EO → Complexation

EO of Polyoxyethylene Alkyl Ether



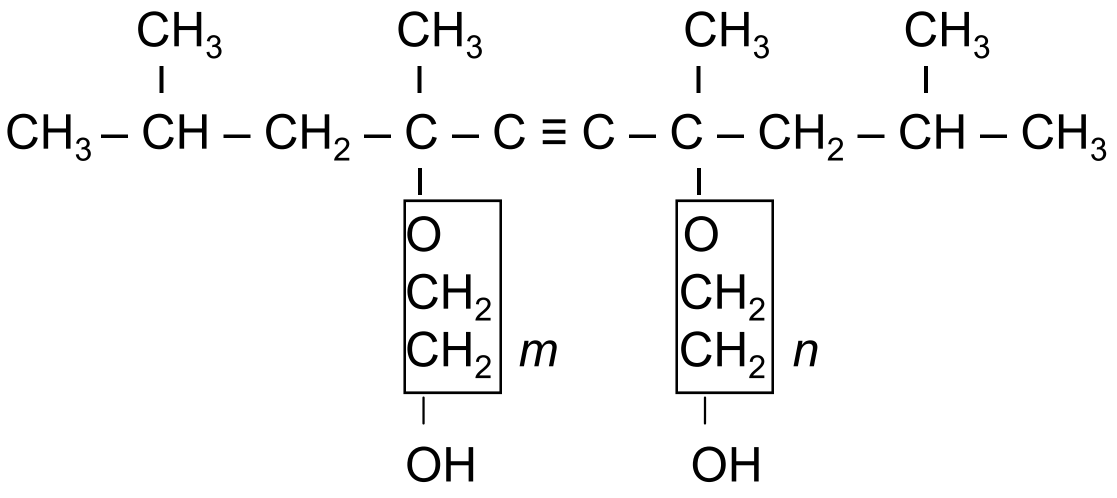
The EO chain locked by the cation, stabilzed by electron-rich oxygen atoms, decreases mobility



Crack tip blunting effects suppressed by shielding of potassium ion.

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

Nonionic Surfactants: Surfynol 400 Series



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{\underset{OH}{|}}{\underset{\boxed{O\,CH_2\,CH_2}\,m}{\overset{CH_3}{\overset{|}{C}}}}-C\equiv C-\underset{\underset{OH}{|}}{\underset{\boxed{O\,CH_2\,CH_2}\,n}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

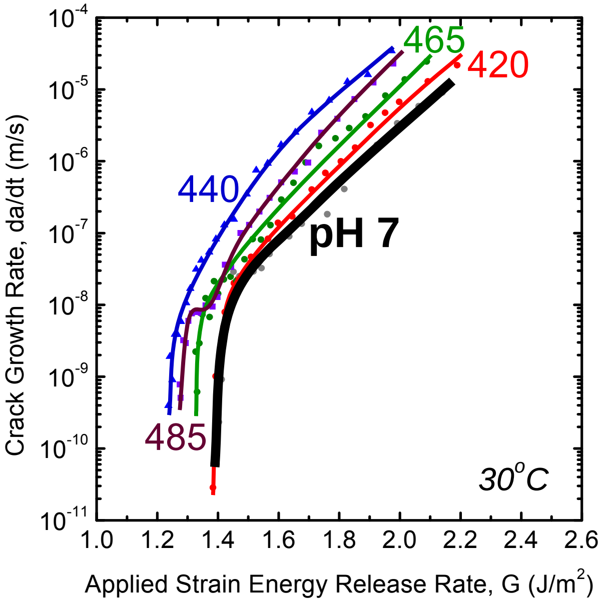
- Dimeric (Gemini) surfactant
- Low foaming (defoaming) and rapid surface wetting

m + *n* = number of moles of ethylene oxide (EO)

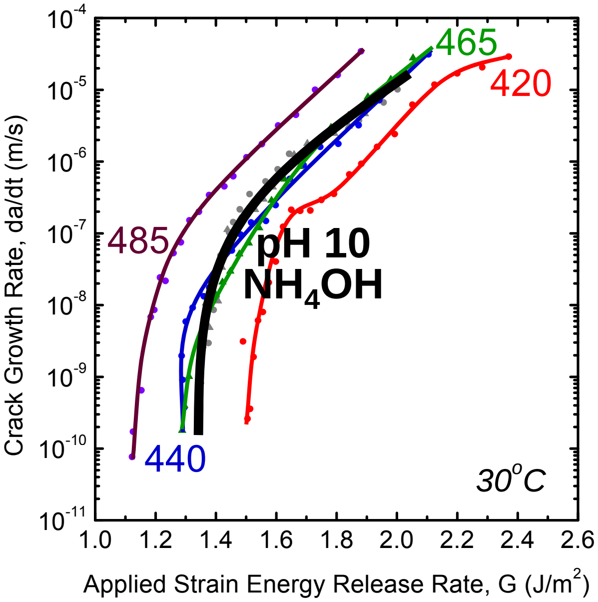
Commercial name	**Surfynol 420**	**Surfynol 440**	**Surfynol 465**	**Surfynol 485**
Ethylene Oxide Content				
Moles	1.3	3.5	10	30
Percent by Weight	20	40	65	85
Specific Gravity @ 25˚C	0.943	0.982	1.038	1.068
HLB	4	8	13	17
VOC (Volatile Organic Compound) Content (wt %)	28	4	<0.01	<0.01
Molecular weight (g/mol)	284	381	667	1548
Molarity of 0.1wt% surfactant solution (M)	3.53×10^{-3}	2.63×10^{-3}	1.50×10^{-3}	6.46×10^{-4}

Nonionic Gemini (Dimeric) Surfactants Effects on Crack Growth Behavior

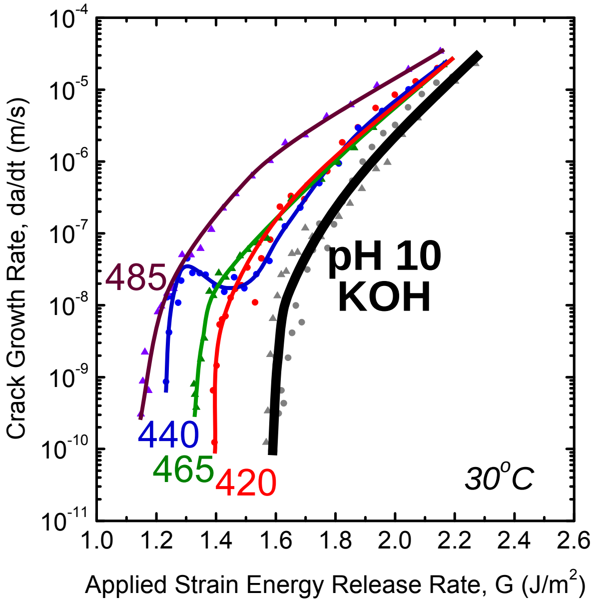
pH 7 + 0.1wt% surfactant



pH10 NH_4OH + 0.1wt% surfactant



pH10 KOH + 0.1wt% surfactant



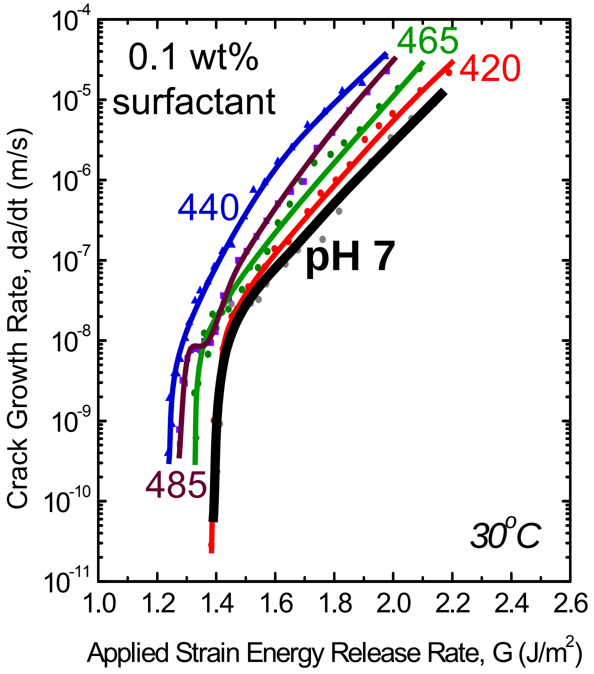
EO length: S420 < S440 < S465 < S485

Low foaming (defoaming) and rapid surface wetting

→ accelerated crack growth

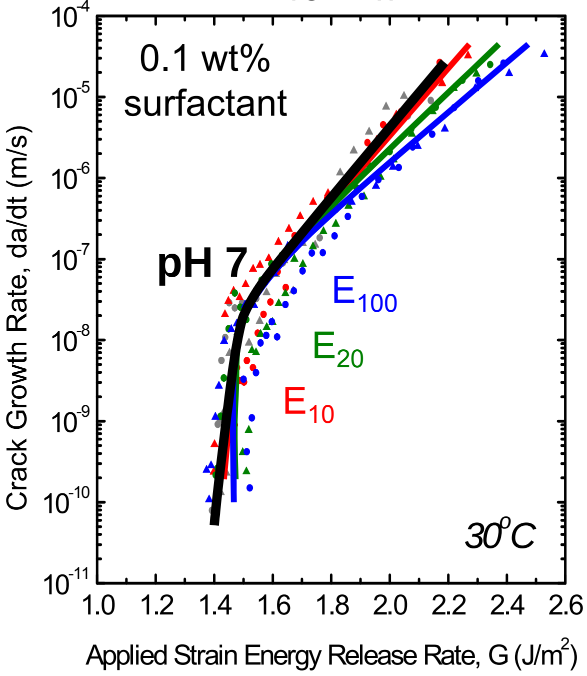
Controlling Crack Growth Rate by Surfactant

Dimeric surfactant



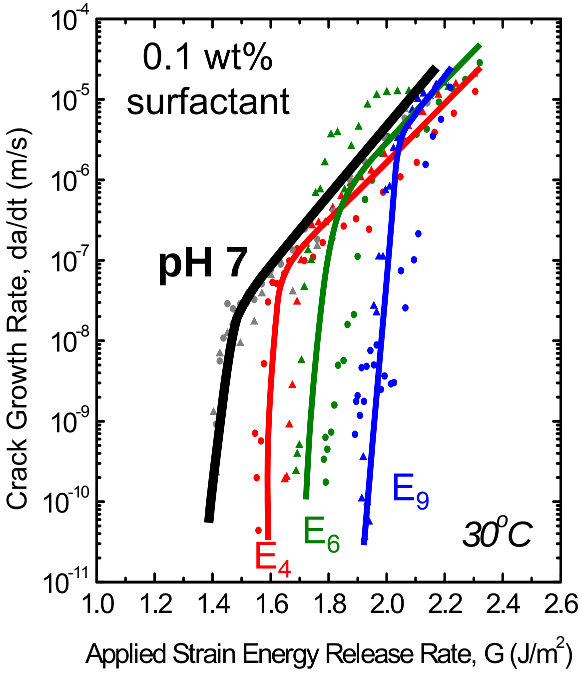
Accelerated crack growth

C_{18} E_n



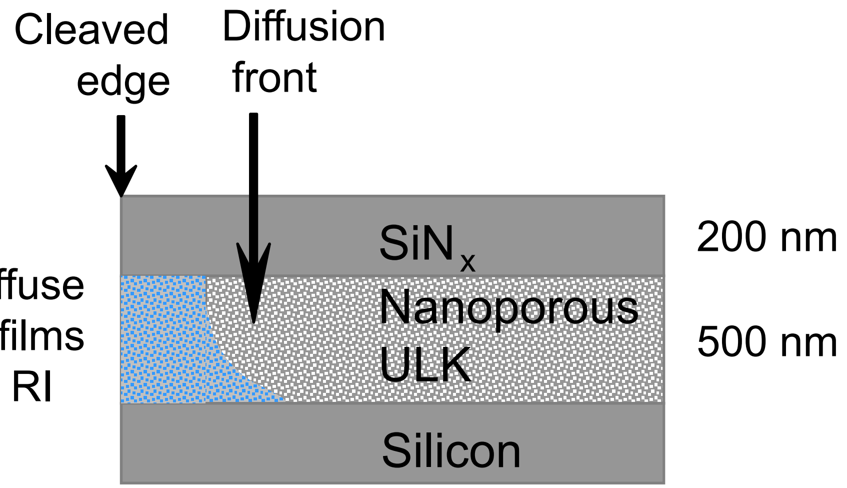
No effect of surfactant additions

C_{10} E_n



Suppressed crack growth

Diffusion of Aqueous Surfactant Solutions into MSSQ



Cleaved edge

Diffusion front

SiN_x

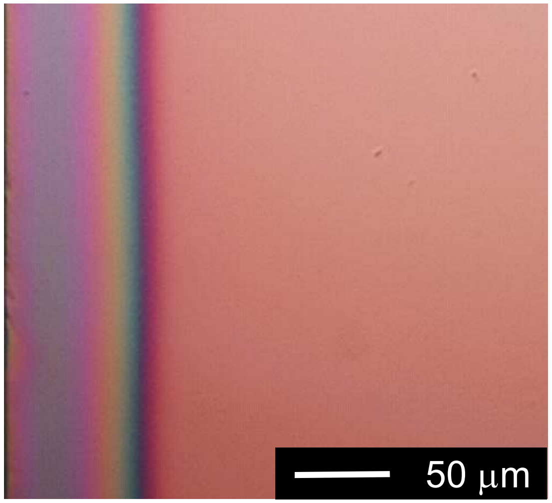
200 nm

Nanoporous ULK

500 nm

Silicon

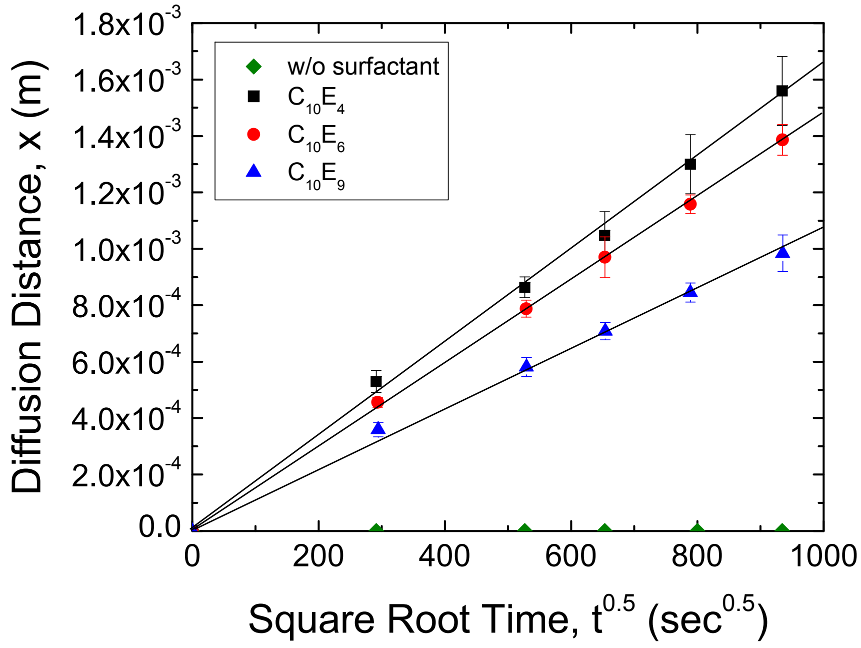
Solutions diffuse into porous films
→ change RI



Diffusion of Aqueous Surfactant Solution

(pH 7 NH_4OH + 0.1wt% $C_{10}E_n$)

$$x = \sqrt{Dt}$$

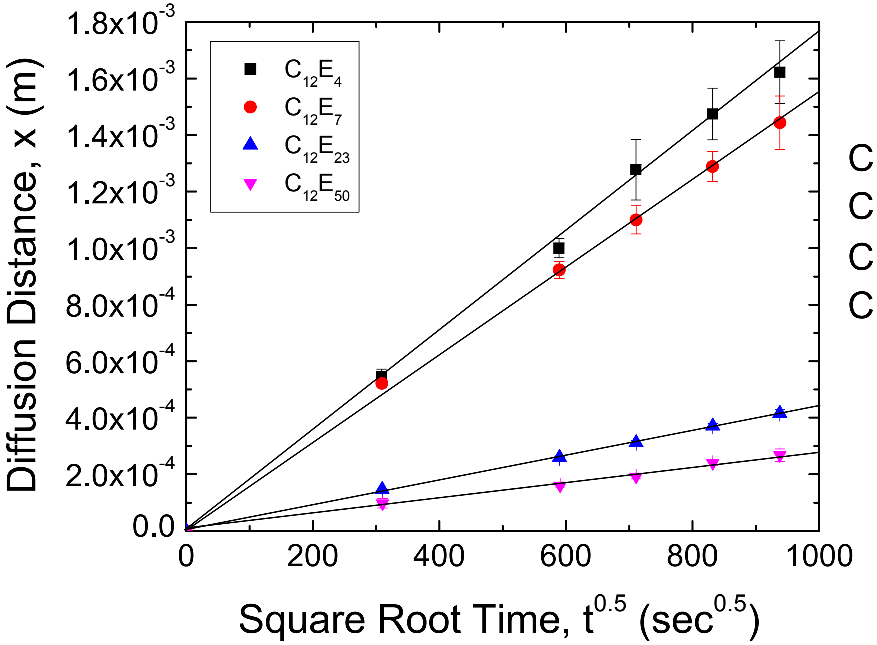


$C_{10}E_4$ (HLB = 10.5)
$C_{10}E_6$ (HLB = 12.4)
$C_{10}E_9$ (HLB = 14.3)

Increasing HLB and MW

Diffusion of Aqueous Surfactant Solution

(pH 7 NH_4OH + 0.1wt% $C_{12}E_n$)

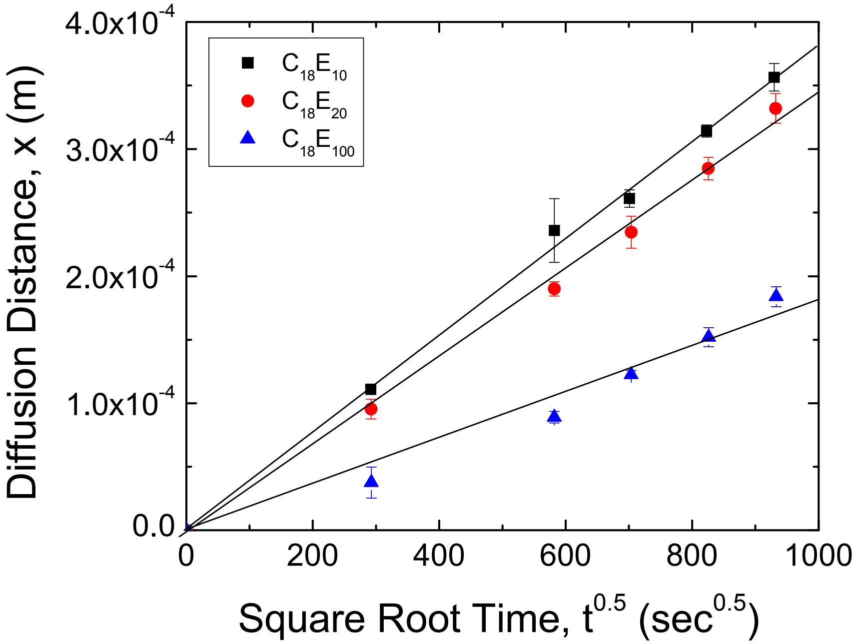


$C_{12}E_4$ (HLB = 9.2)
$C_{12}E_7$ (HLB = 12.2)
$C_{12}E_{23}$ (HLB = 16.8)
$C_{12}E_{50}$ (HLB = 18.3)

Increasing HLB and MW

Diffusion of Aqueous Surfactant Solution

(pH 7 NH_4OH + 0.1wt% $C_{18}E_n$)



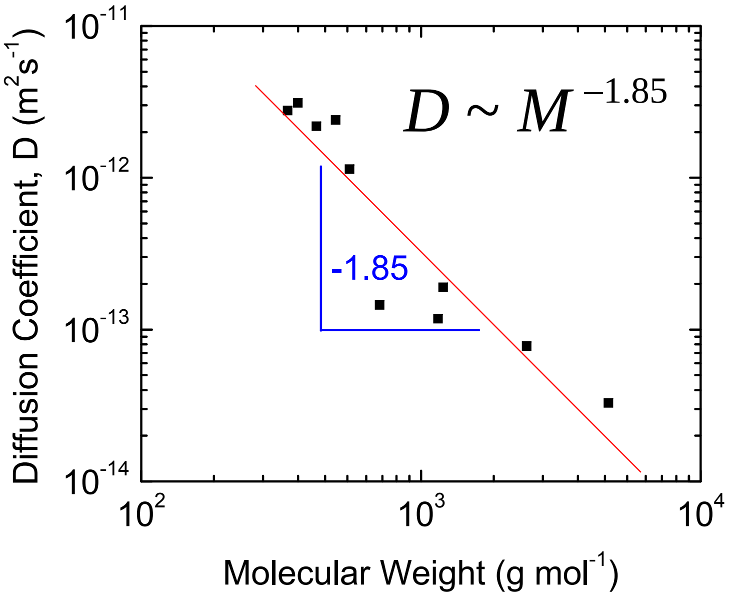
$C_{18}E_{10}$ (HLB = 12.4)
$C_{18}E_{20}$ (HLB = 15.3)
$C_{18}E_{100}$ (HLB = 18.8)

Increasing HLB and MW

Diffusion Coefficient (pH 7 NH_4OH + 0.1wt% C_mE_n)

Commercial name	**# of C, *m***	**# of EO, *n***	**HLB**	**Molecular weight, M (g/mol)**	**Diffusion coefficient, D (m^2s^{-1})**
ETHALL DA-4	10	4	10.5	334	2.77E-12
DA-6		6	12.4	423	2.19E-12
DA-9		9	14.3	555	1.14E-12
ETHALL LA-4	12	4	9.2	363	3.12E-12
LA-7		7	12.2	495	2.4E-12
LA-23		23	16.8	1200	1.9E-13
LA-50		50	18.3	2389	7.8E-14
BRIJ 76	18	10	12.4	711	1.45E-13
78		20	15.3	1152	1.18E-13
700		100	18.8	4676	3.28E-14

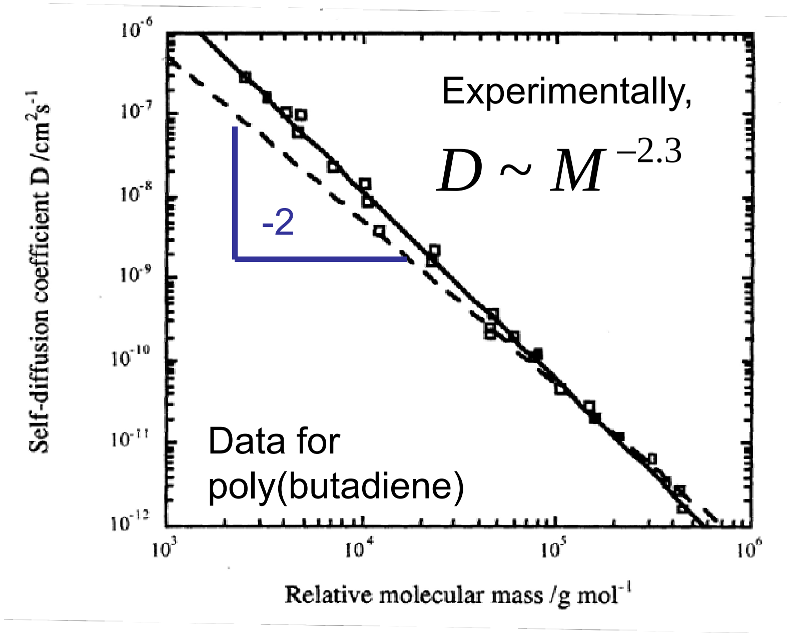
$$x = \sqrt{Dt}$$



Polymer Reptation Theory

Polymer self-diffusion in polymer melts

$$D \sim M^{-2}$$



Experimentally,

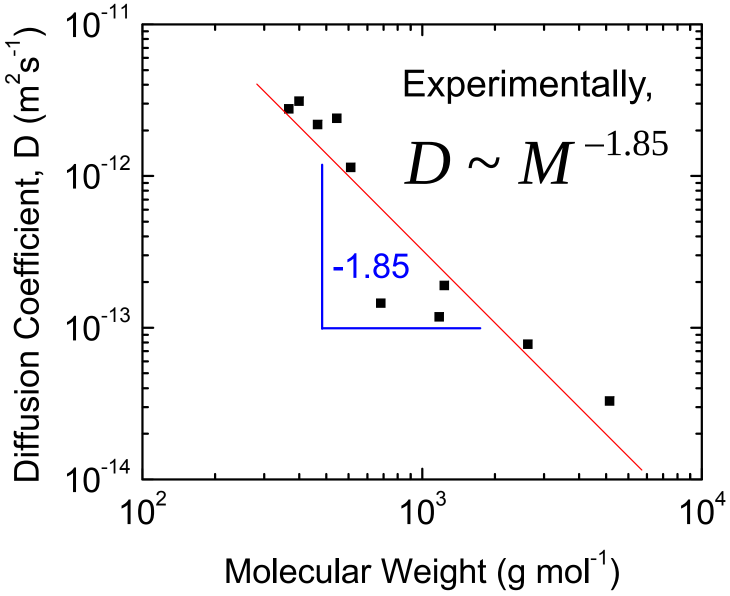
$$D \sim M^{-2.3}$$

Data for poly(butadiene)

Jones, *Soft Condensed Matter*, p. 92

Aqueous surfactant solution diffusion in nanoporous MSSQ

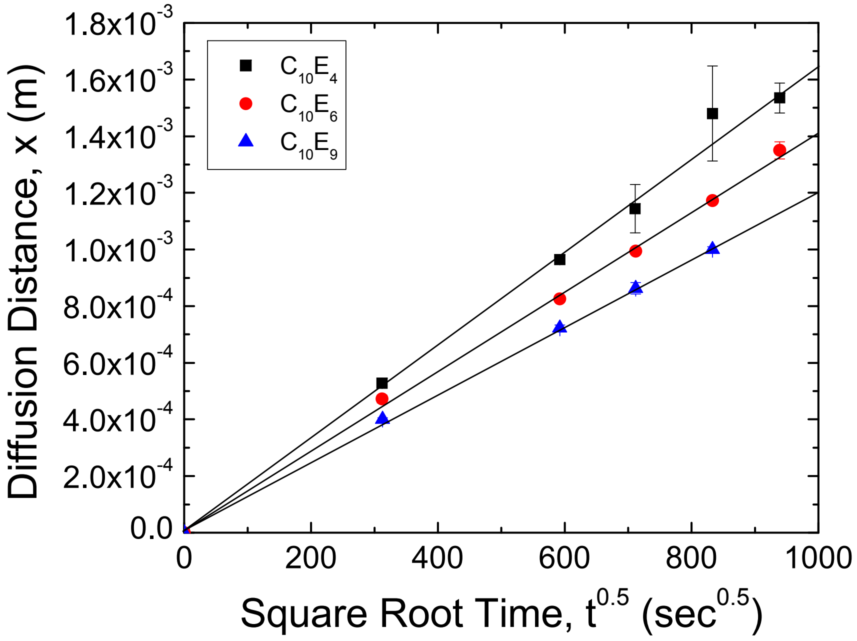
$$D \sim M^{-2} \quad ?$$



Experimentally,

$$D \sim M^{-1.85}$$

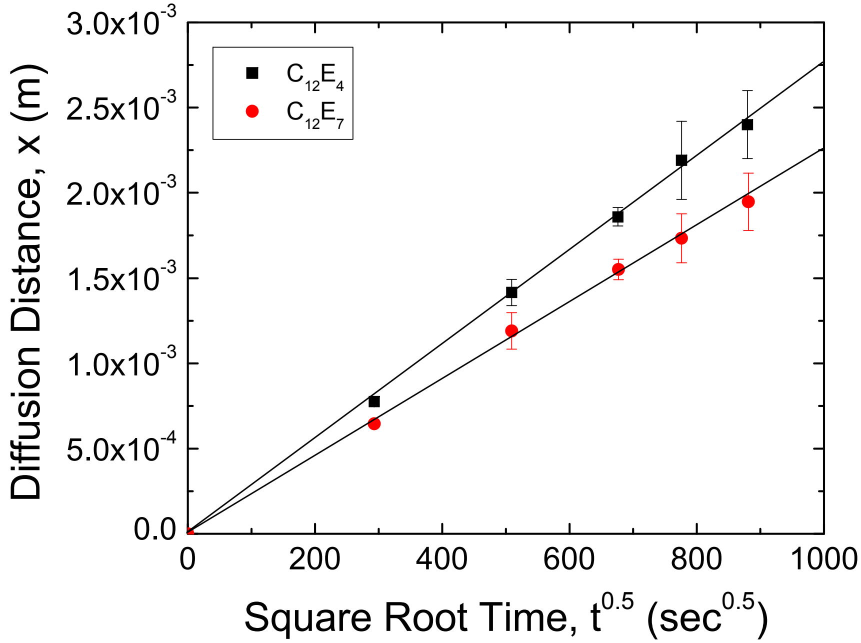
Diffusion of Pure Surfactant in Liquid Phase ($C_{10}E_n$)



$C_{10}E_4$ (HLB = 10.5)
$C_{10}E_6$ (HLB = 12.4)
$C_{10}E_9$ (HLB = 14.3)

Increasing HLB and MW

Diffusion of Pure Surfactant in Liquid Phase ($C_{12}E_n$)



$C_{12}E_4$ (HLB = 9.2)
$C_{12}E_7$ (HLB = 12.2)

Increasing HLB and MW

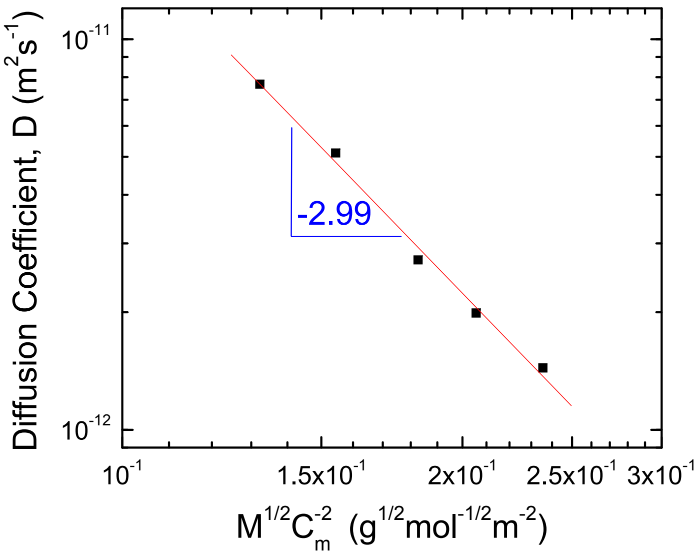
Diffusion Coefficient (100wt% pure surfactant)

0.1wt% 100wt%

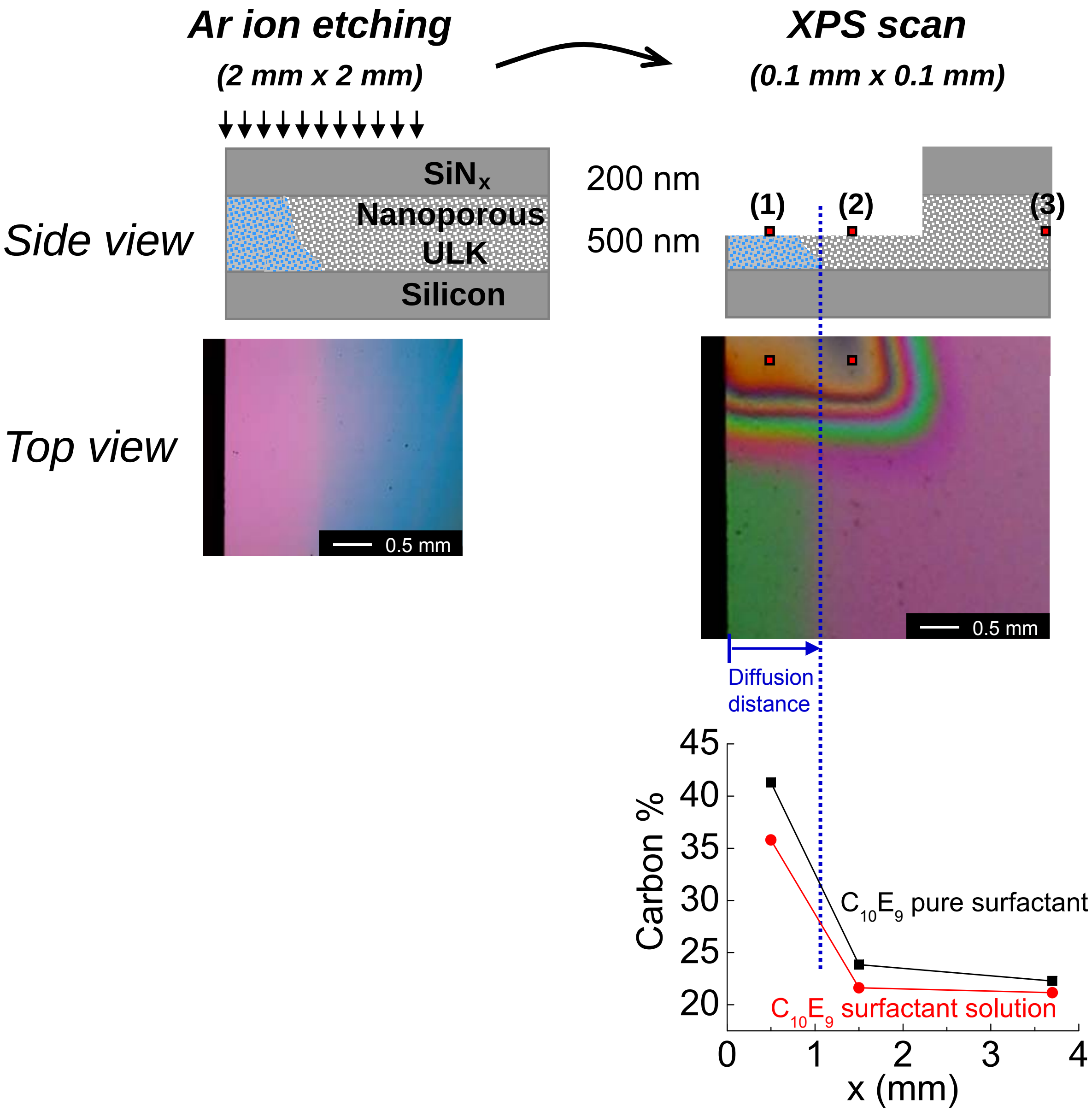
Commercial name	# of C, *m*	# of EO, *n*	HLB	Molecular weight, M (g/mol)	Diffusion coefficient, D (m^2s^{-1})	Diffusion coefficient, D (m^2s^{-1})
ETHALL DA-4	10	4	10.5	334	2.77E-12	2.72E-12
DA-6		6	12.4	423	2.19E-12	1.99E-12
DA-9		9	14.3	555	1.14E-12	1.44E-12
ETHALL LA-4	12	4	9.2	363	3.12E-12	7.67E-12
LA-7		7	12.2	495	2.4E-12	5.11E-12
LA-23		23	16.8	1200	1.9E-13	
LA-50		50	18.3	2389	7.8E-14	
BRIJ 76	18	10	12.4	711	1.45E-13	
78		20	15.3	1152	1.18E-13	
700		100	18.8	4676	3.28E-14	

Hydrophobic tail length

$$D \sim [M^{1/2} C_m{}^{-2}]^{-3}$$



Increase of Carbon Content by Surfactant Diffusion



Atom %

$C_{10}E_9$ pure surfactant in liquid phase

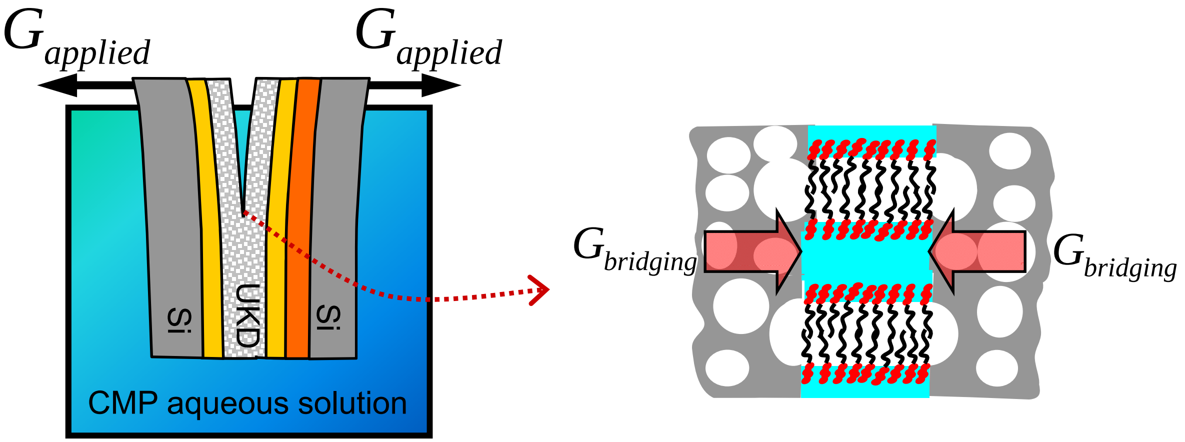
	(1)	(2)	(3)
O	27.97	42.88	47.82
C	41.30	23.84	22.27
Si	30.73	33.28	29.90

pH7 NH_4OH DI water + 0.1wt% $C_{10}E_9$

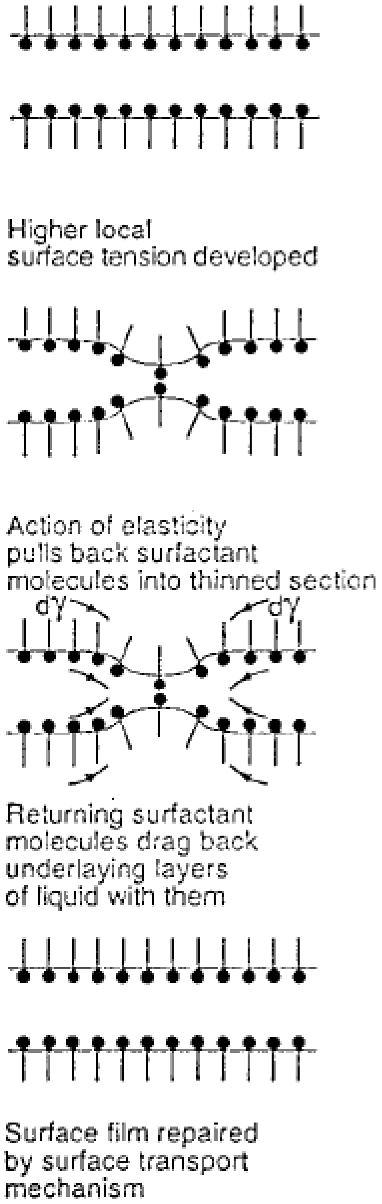
	(1)	(2)	(3)
O	36.63	45.76	46.01
C	35.80	21.61	21.15
Si	27.57	32.63	32.84

Gibbs-Marangoni Effects

In foams, the Gibbs-Marangoni effect provides a resisting force to the thinning of liquid films.



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



Higher local surface tension developed

Action of elasticity pulls back surfactant molecules into thinned section

Returning surfactant molecules drag back underlaying layers of liquid with them

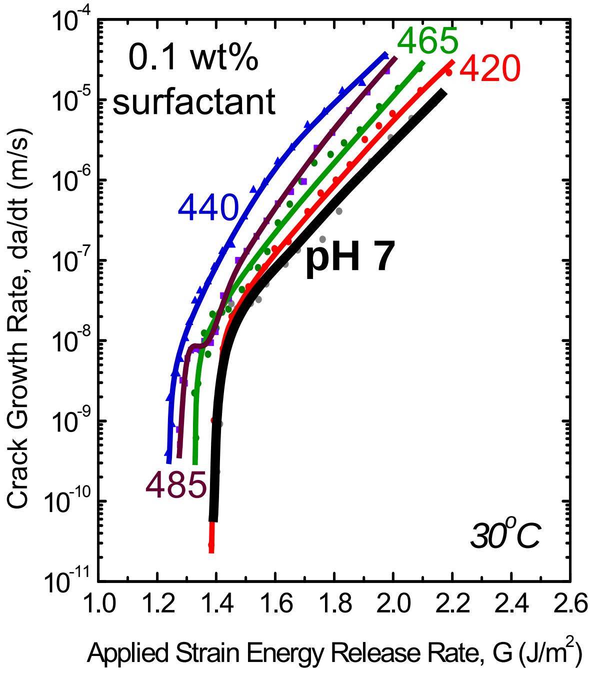
Surface film repaired by surface transport mechanism

Schramm, 2000

Conclusion

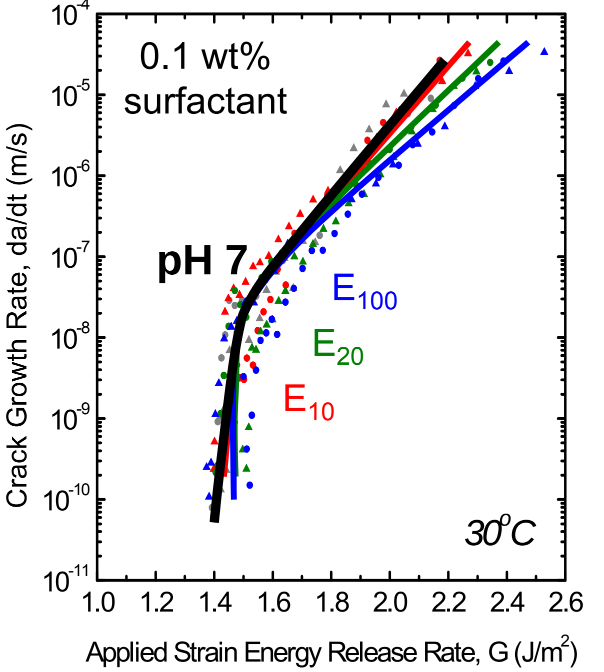
- The growth of damage is a kinetic process involving stress <u>*and*</u> the presence of active chemical species.
- Careful surfactant additions can control the defect evolution.

Dimeric surfactant



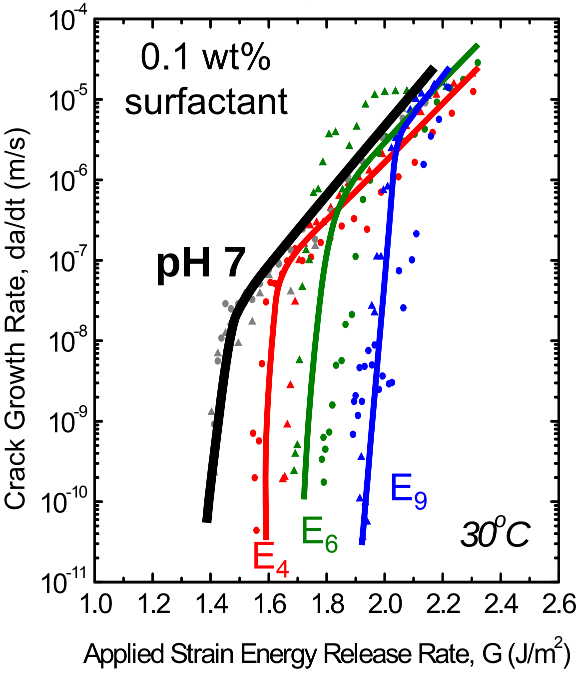
Accelerated crack growth

$C_{18}\ E_n$



No effect of surfactant additions

$C_{10}\ E_n$



Suppressed crack growth

Thank you!

Q&A

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