

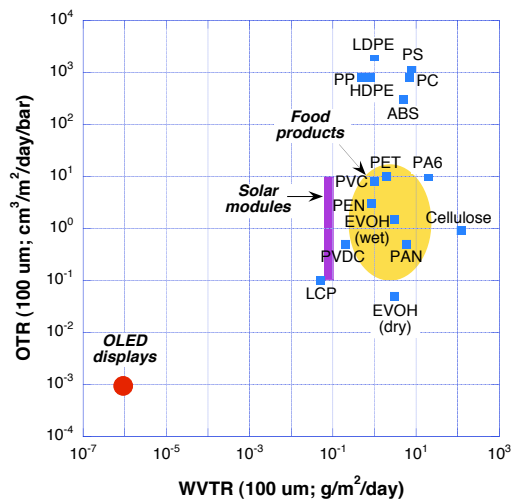
# Encapsulation of Organic Photonic Elements

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SwissLaser Net Workshop, Basel, June 25, 2008

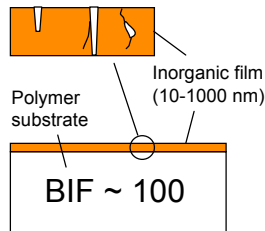
## Polymers are (too) permeable



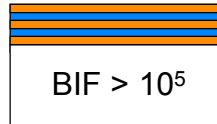
Crank & Park, 'Diffusion in polymers' Academic Press (1968)  
Chatam, Surf. Coat. Technol. (1996)  
Pauly, in 'Polymer Handbook' Wiley (1999)

## High-Barrier Strategies

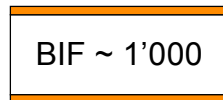
**Barrier Improvement Factor:  $BIF = P_s/P$**



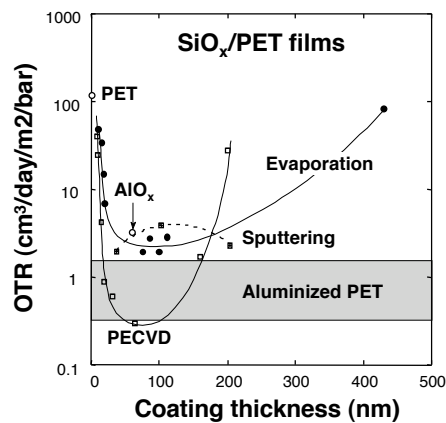
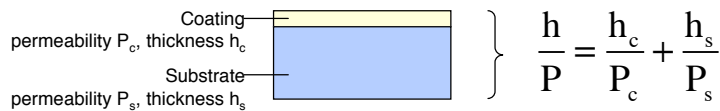
*nanolaminates*



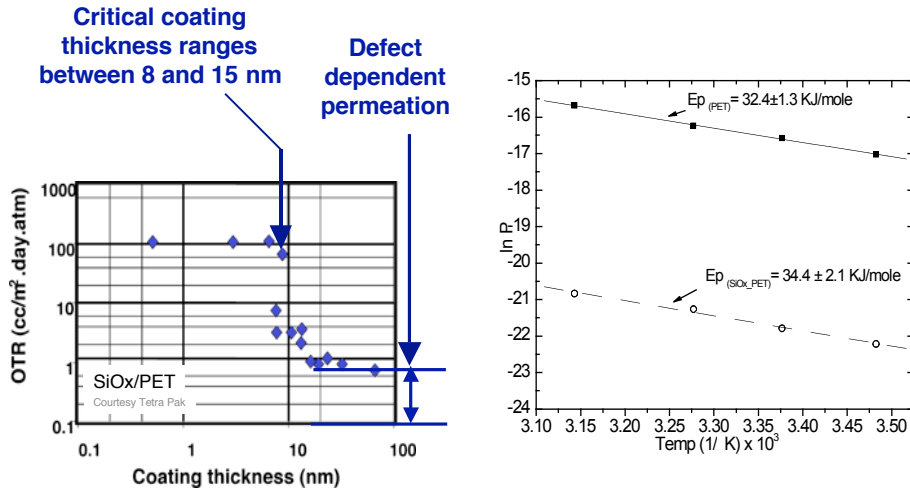
*Organic-inorganic hybrids*



## Nanosized inorganic coatings/polymer composites

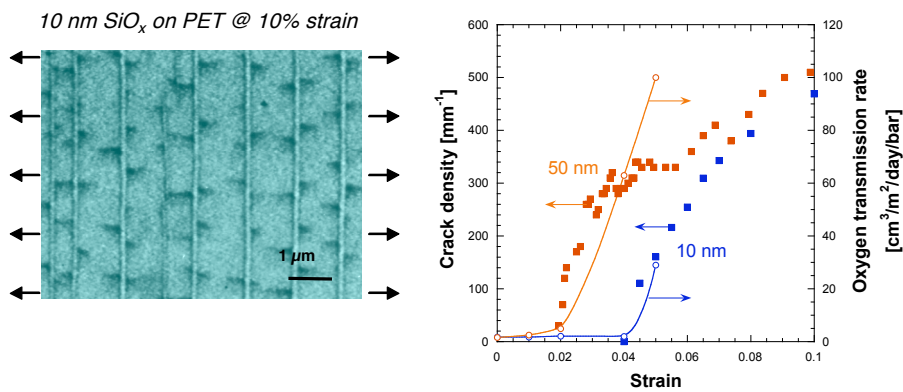


## Defects in vapor-deposited inorganic films on polymers



Roberts et al., J. Membrane Sci. (2002)  
 Rochat, Leterrier, Manson, Fayet, Surf. Coat Technol. (2003, 2006)

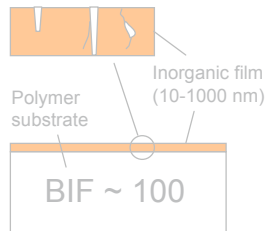
## Effect of coating defects on failure of barrier



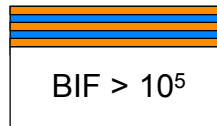
Rochat, Leterrier et al., J. Appl. Phys. (2003)  
 Singh, Leterrier, Manson, Fayet, Surf. Coat. Technol. (2007)

## High-Barrier Strategies

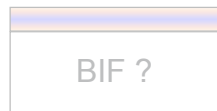
Barrier Improvement Factor:  $BIF = P_s/P$



nanolaminates

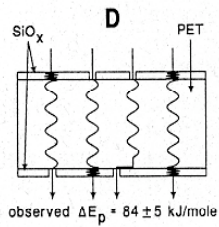
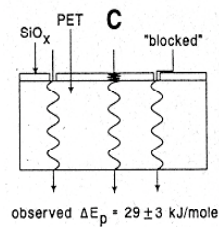
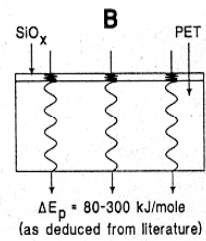
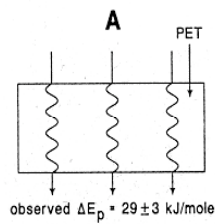
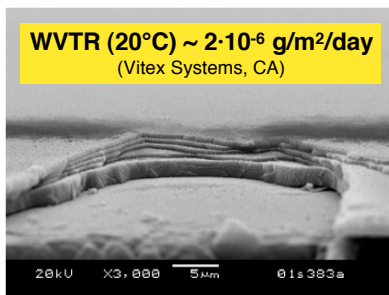
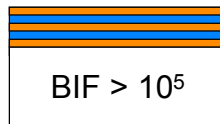


Organic-inorganic hybrids



## Why nanolaminate structures?

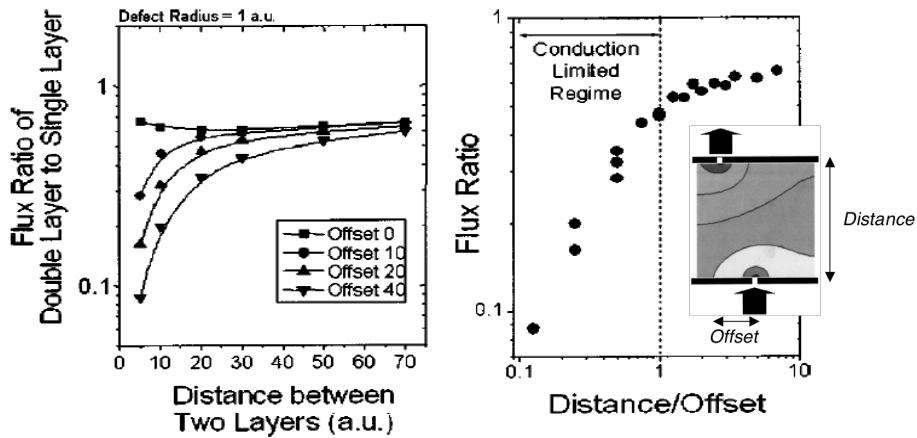
Nanolaminates decouple defect structure



Trophsa & Harvey, J. Phys. Chem. B (1997)

## Modeling of gas transport

Barrier improvement obtained when adding a second inorganic layer



Trophsa & Harvey, J. Phys. Chem. B (1997)  
Schaepekens et al., J. Vac. Sci. Technol (2004)

Y. Leterrier - SwissLaser Net Workshop, Basel, June 25, 2008

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## Nanolaminate encapsulation

Producer	Encapsulation Structure	Number of layers	W V T R (g.m <sup>-2</sup> .day)	Crack Onset Strain (%)
Vitex (Barix)	[acrylate/Al <sub>2</sub> O <sub>3</sub> ] <sub>n</sub>	10	~ 1 × 10 <sup>-6</sup>	0.8
Philips (NONON)	[SiN <sub>x</sub> /SiO <sub>2</sub> ] <sub>n</sub>	'12' + topcoat	3.6 × 10 <sup>-6</sup>	1.0
GE (graded UHB)	[SiN <sub>x</sub> /SiO <sub>2</sub> ] <sub>n</sub>	'5'	8.6 × 10 <sup>-6</sup>	-
Applied Materials	(SiN/lacquer) <sub>2</sub>	4	~ 1 × 10 <sup>-5</sup>	1.0

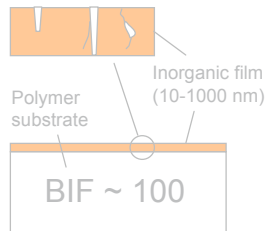
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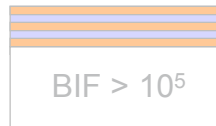
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## High-Barrier Strategies

Barrier Improvement Factor:  $BIF = P_s/P$



*nanolaminates*

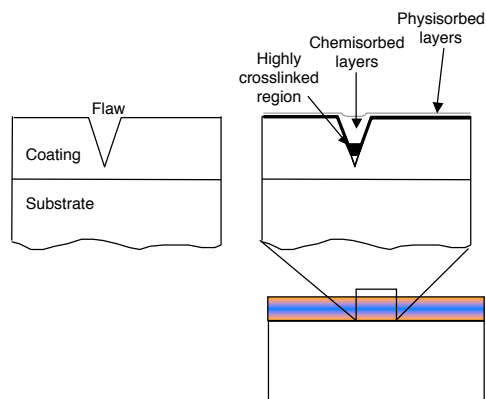
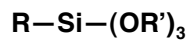


*Organic-inorganic hybrids*



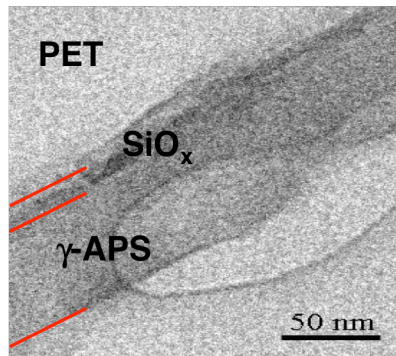
## Why organic-inorganic hybrids?

Organo-silanes reduce the severity of superficial defects ('Griffith flaws')



## Processing of organosilane-silica hybrids

SiO<sub>x</sub> 12 nm PECVD from O<sub>2</sub> diluted HMDSO on 12 μm thick PET web  
 OTR ~ 2.1 cm<sup>3</sup>/m<sup>2</sup>/day/bar  
 COS ~ 3.5%



Magni et al., *J. Phys. D* (2001)  
 Bouchet, Leterrier et al., *Surf. Coat. Technol.* (2005, 2007)

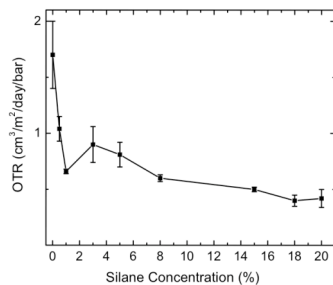
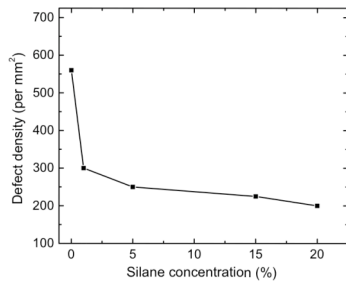
NH2-CH2-CH2-CH2-Si(OC2H5)3  
 Gamma-aminopropyltriethoxysilane  
 (γ-APS, Silquest A-1100™)

1 - 20 %wt γ-APS/ethanol  
 pH=11.4 and pH=8 (acetic acid)

Spin coating on SiO<sub>x</sub>/PET films  
 1000 rpm, 20 s

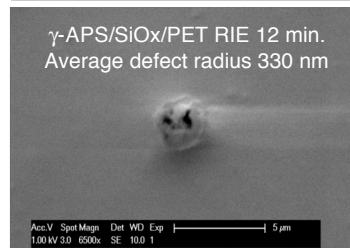
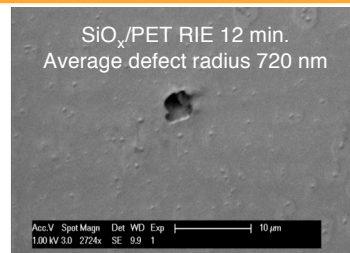
oligomerization: 12 h at 60°C  
 10 - 500 nm thick silane films

## Defect analysis in organosilane-silica hybrids

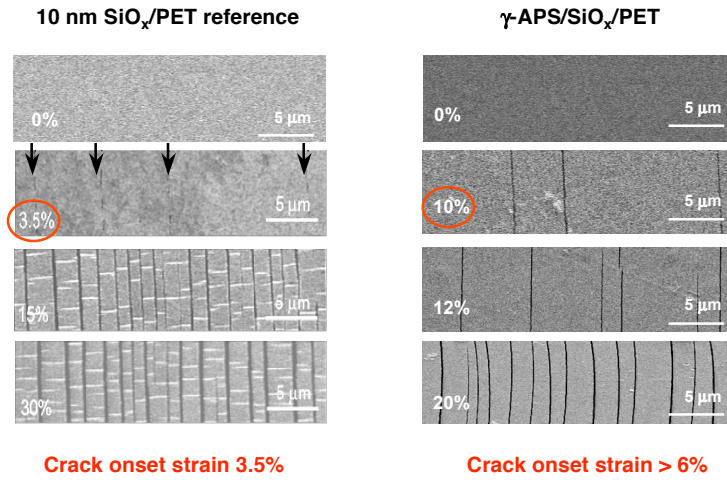


Singh, Leterrier et al., *Surf. Coat. Technol.* (2007)

**Amino-silane treatment reduces the size and population of macro-defects**



## Mechanical integrity of organosilane-silica hybrids



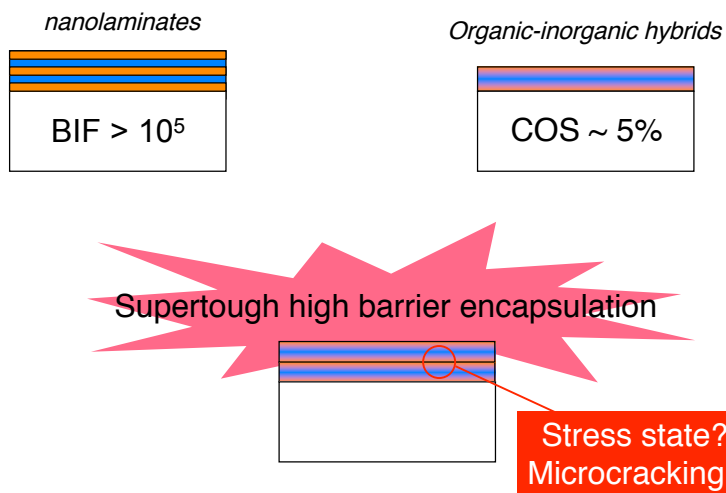
Rochat et al. *Thin Solid Films* (2003)

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## Supertough high barrier encapsulation



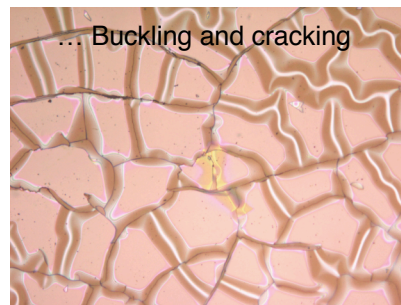
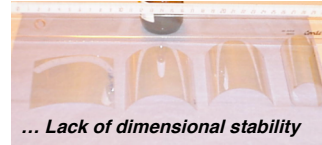
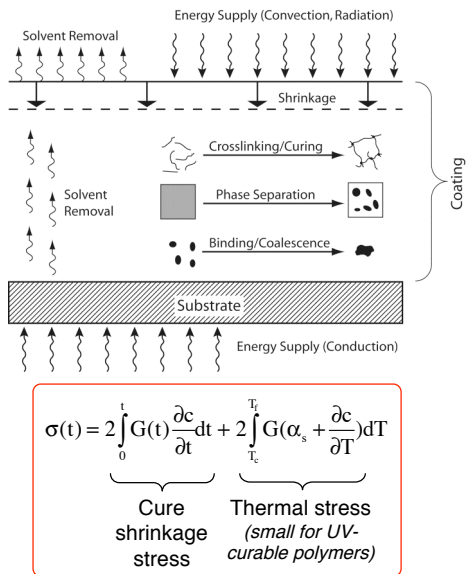
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## Origin of stress in polymer coatings



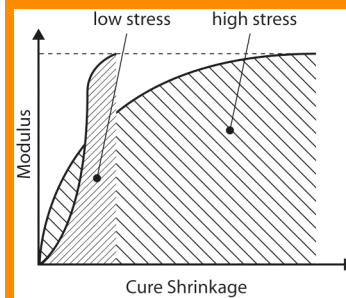
Lange, Manson et al., Polymer (1995, 1997); Payne (1998)

## Towards low stress encapsulation

- Tailored process temperature cycles
- 'Low profile' additives
- Radiation curing
- ...
- Hyperbranched polymers

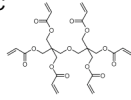
A low-stress material combines:

- **reduced shrinkage**  
⇒ radiation curing
- **retarded modulus build-up**  
⇒ hyperbranched polymers

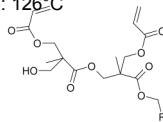


## Low Stress UV Curable Hyperbranched Polymer Nanocomposites

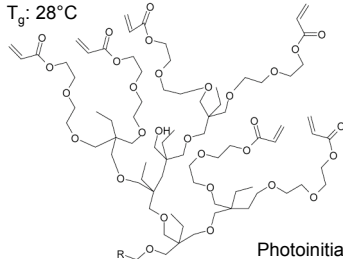
a) Di-Pentaerythritol Hexaacrylate (DPHA)  
T<sub>g</sub>: 68°C



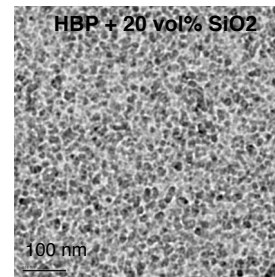
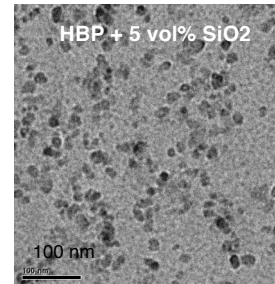
b) Segment of Acrylated Boltorn H20  
T<sub>g</sub>: 126°C



c) Segment of Acrylated Polyether HBP  
T<sub>g</sub>: 28°C

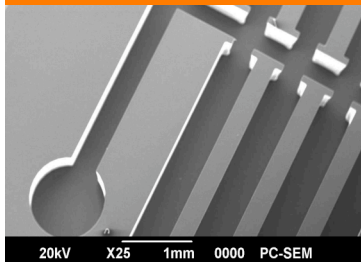


Photoinitiators:  
1-Hydroxy-cyclohexyl-phenyl-ketone  
1:1 blend of 1-Hydroxy-cyclohexyl-phenyl-ketone and benzophenone

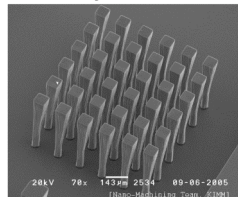


## Low Stress UV Curable Hyperbranched Polymer Nanocomposites

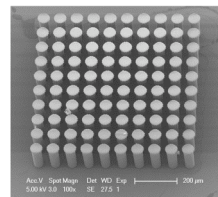
Microbattery, layer thickness 500 µm



Polyether HBP



SU8



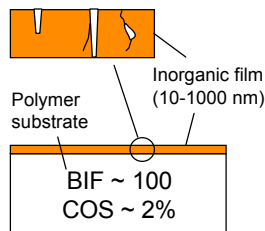
$$FOM = (L \times AR) / (\text{Stress} \times \text{Fab\_Time})$$

Resist	Layer thickness, L (µm)	Aspect ratio, AR	Residual stress (MPa)	Fabrication time (h)	FOM
Polyether HBP	850	7.7	2.4	0.5	5454
Polyester HBP	500	3.3	4.5	0.5	733
SU-8	250	11	25	3	37

Jin Y.-H., J. Micromech. Microeng., 17, 1147-1153 (2007).  
Schmidt et al., J. Micromech. Microeng. 18, 045022 (2008).

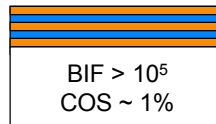
## High-Barrier Strategies

$$\text{Barrier Improvement Factor: } BIF = P_s/P$$



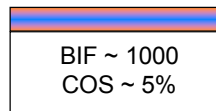
BIF ~ 100  
COS ~ 2%

### nanolaminates

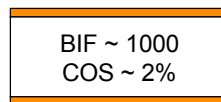


BIF > 10<sup>5</sup>  
COS ~ 1%

### Organic-inorganic hybrids



BIF ~ 1000  
COS ~ 5%



BIF ~ 1000  
COS ~ 2%

## Acknowledgements

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