Combinatorial Measurements of Polymer Adhesion

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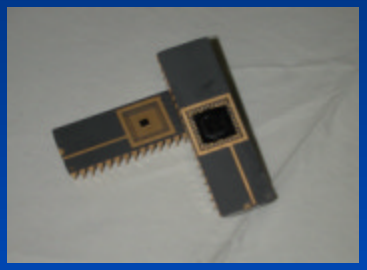
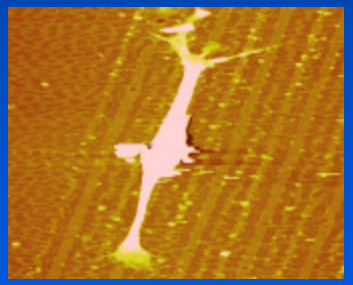
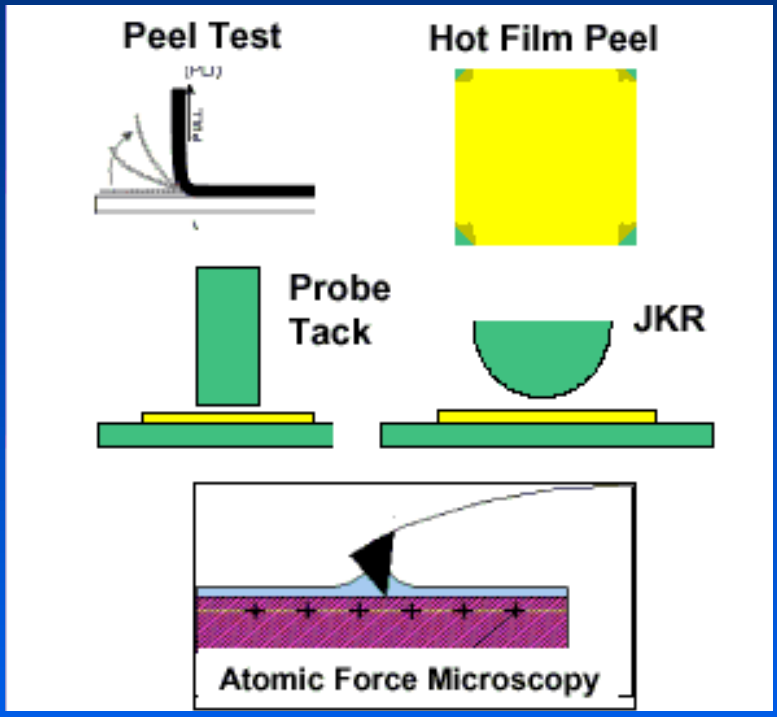
Introduction





… although adhesion is omnipresent, our current understanding of the fundamental mechanism of polymer adhesion is far from complete

Motivation

Industrial

- Many applications involved - such as *electronic packaging, biomedical devices* and *implants, composites*, ….
- Product design and quality control, ….
- Many variables control adhesion and varied existing techniques for measuring adhesion

Scientific issues

- Interface strength/stability between polymer and non-polymer, including metal, ceramics, …
- Molecular chain diffusion, bond generation, ….

Objective

Develop & ***test*** methodologies for quantitative high-throughput measurement of adhesive strength of polymer interface

Outline

Methods

Polymer Debonding
Peel-off Test

Test Systems

Stress gradient on PMMA adhesion
Temperature effects on adhesion (T_g, Gradient)
Surface energy gradient on PMMA adhesion
Gradient UV-exposure on PMMA stability
Casting-solvent effect on PMMA adhesion
Material aspects (different tapes, metals)
Tape adhesion on surface energy gradient

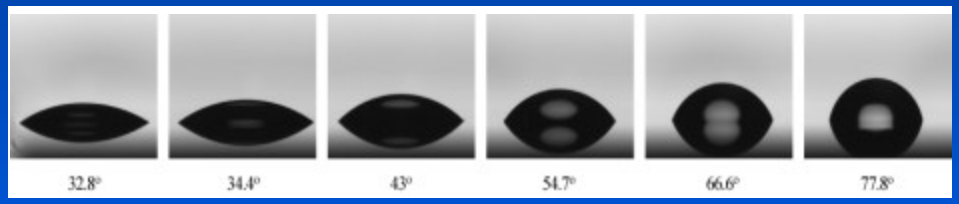
Why select PMMA

- Widely used in industries such as microelectronics
- Easily prepared into uniform solution
- Relatively stable upon heating & without crystallization
- Wide visible- and UV-absorbance range

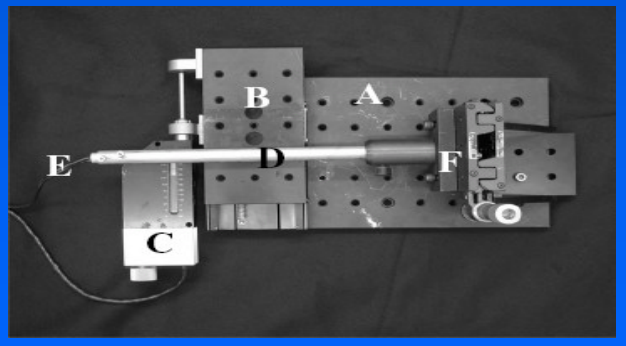
Gradient Methods Used

Thermal gradient

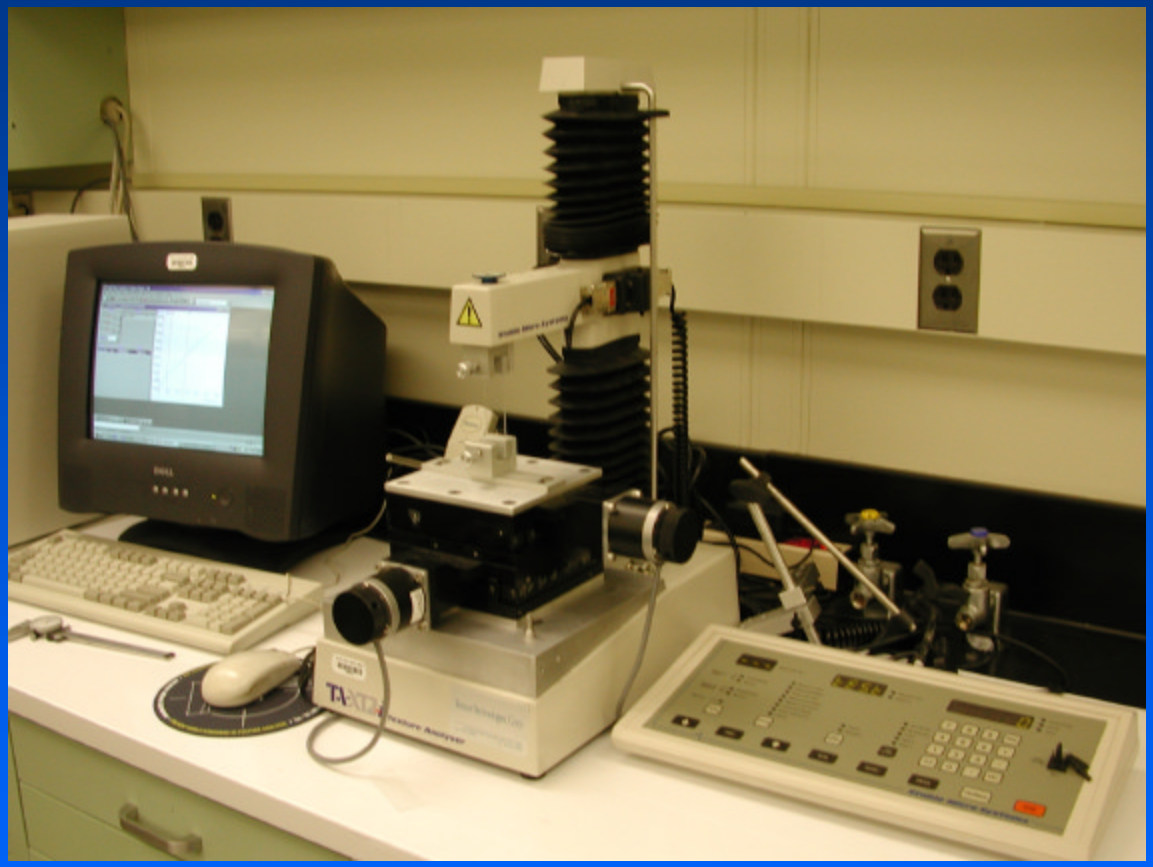
Contact angle gradient



UV exposure gradient



Peel-off Test (mini-Instron)



Control:

Peel-off Rate

Measure:

Force (Peel-off Position)

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Simultaneous Thickness & Surface Energy Gradient on PMMA adhesion

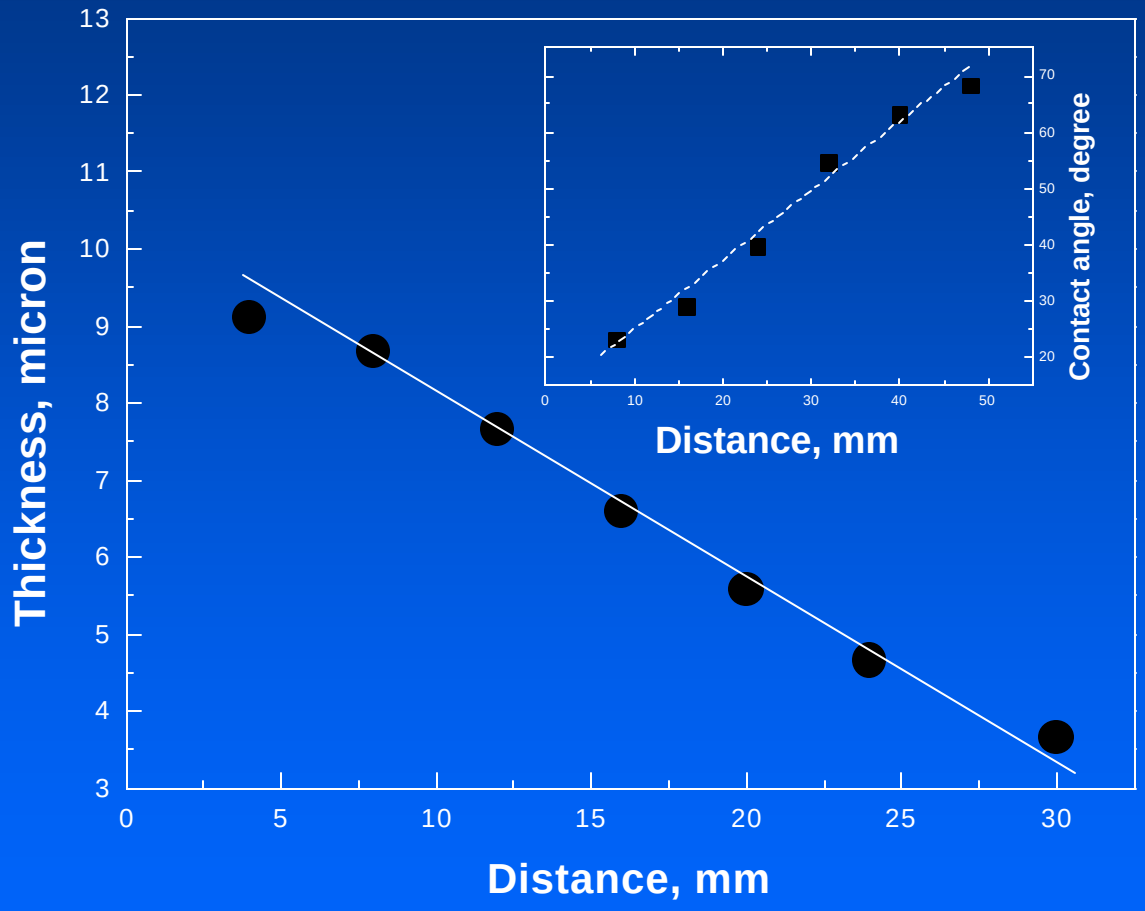
National Institute of Standards and Technology

Create 2-D Orthogonal Gradients

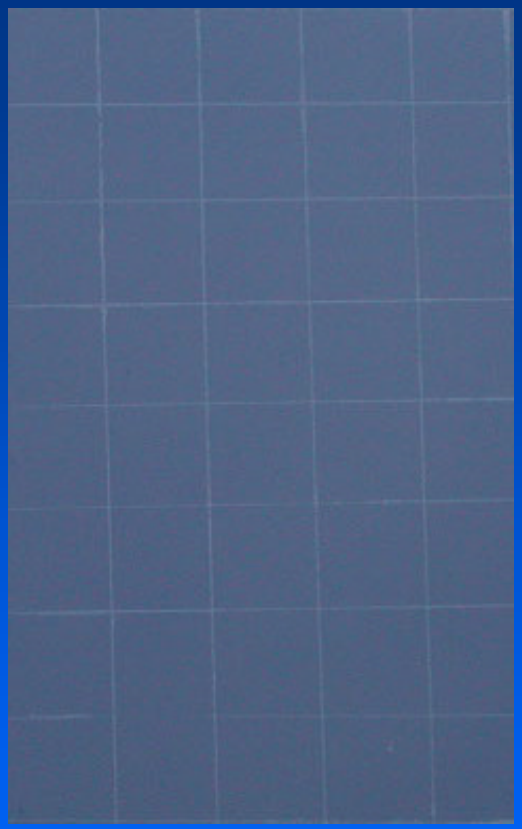
Thickness Gradient (Induces PMMA/Si Thermal Expansion Mismatch Stress Gradient):
Flow coater gradient

Contact Angle Gradient (Affects Adhesion):
SAM layer irradiated by UV

Orthogonal Gradients- Contact Angle and Thickness of PMMA Film



Combinatorial Measurement of Polymer Adhesion

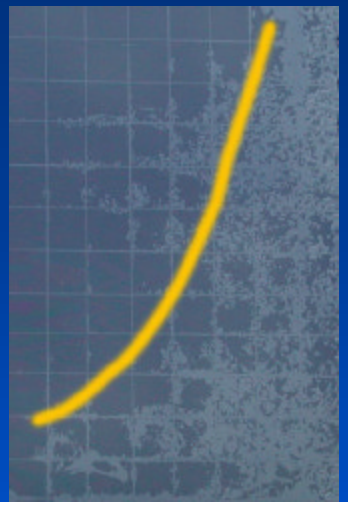


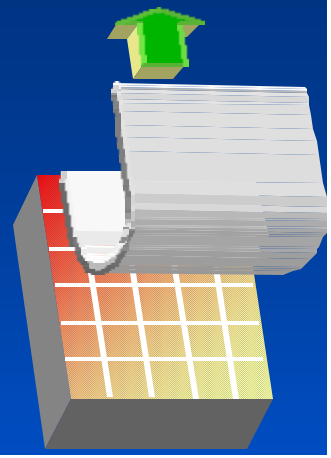
Hydrophilicity increase (70 - 30 degree)

Thickness increase

(3-11 micron)

After peel-off test

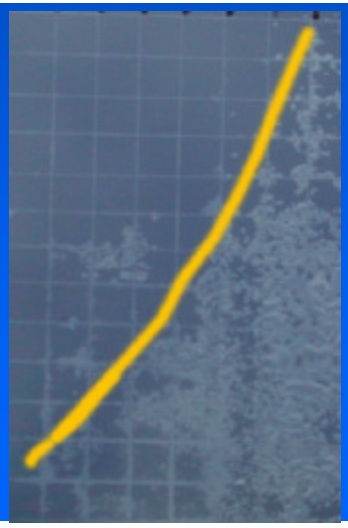




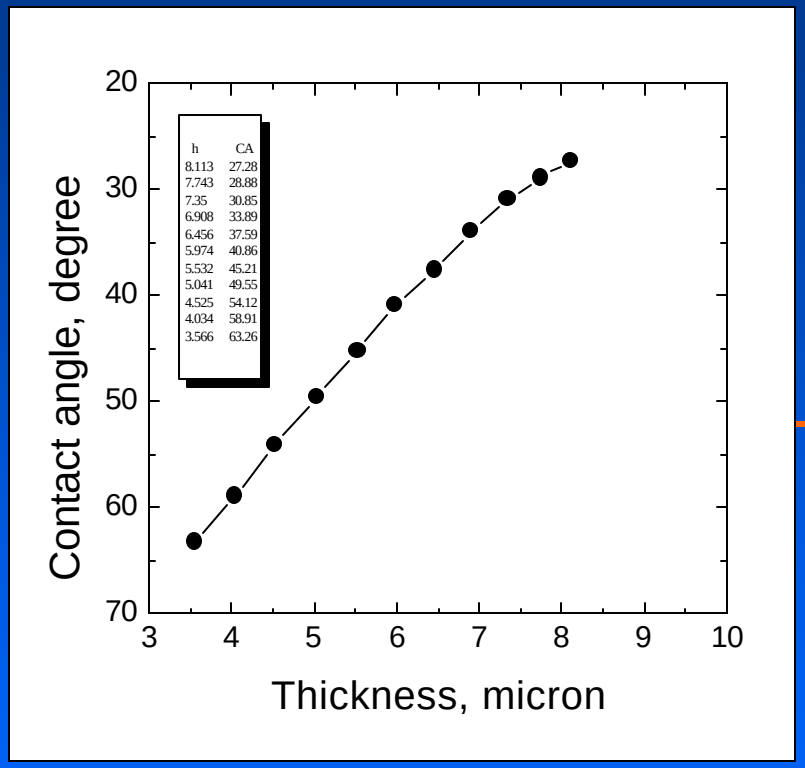
180º Peel Test on Combinatorial Libraries

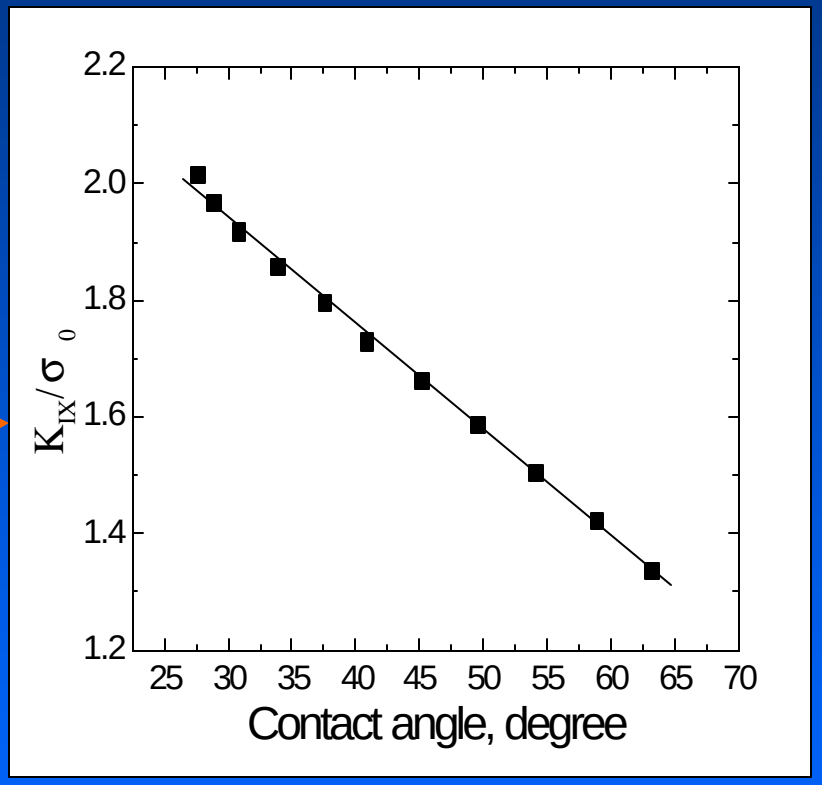
After thermal cooling

(Liquid Nitrogen for 5 sec.)



Critical Thickness and Contact Angle for PMMA Thin Film





(Martin Chiang)

PMMA Films with Single Gradient

(After Annealed Below or Above its T_g)

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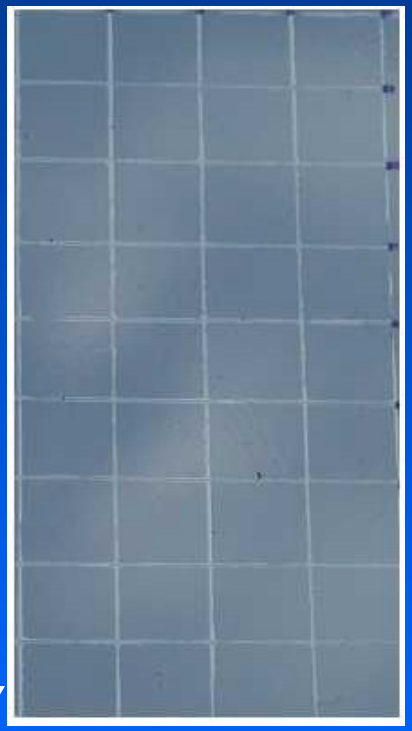
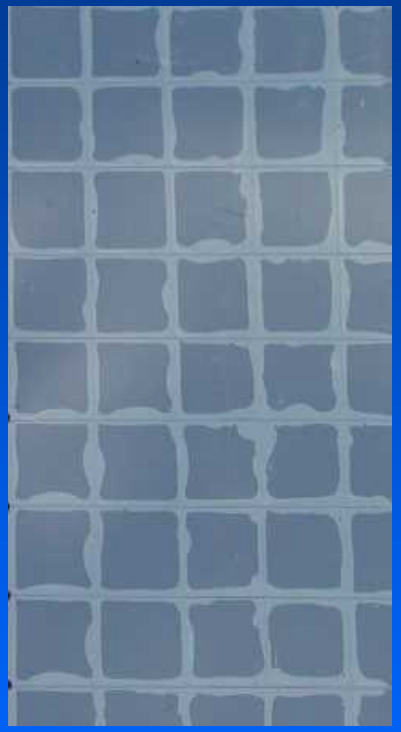
Thickness gradient

Contact angle gradient

70°C for 64 h, spin coating PMMA layer, ca. 240 nm



140°C for 20 h, spin coating PMMA layer

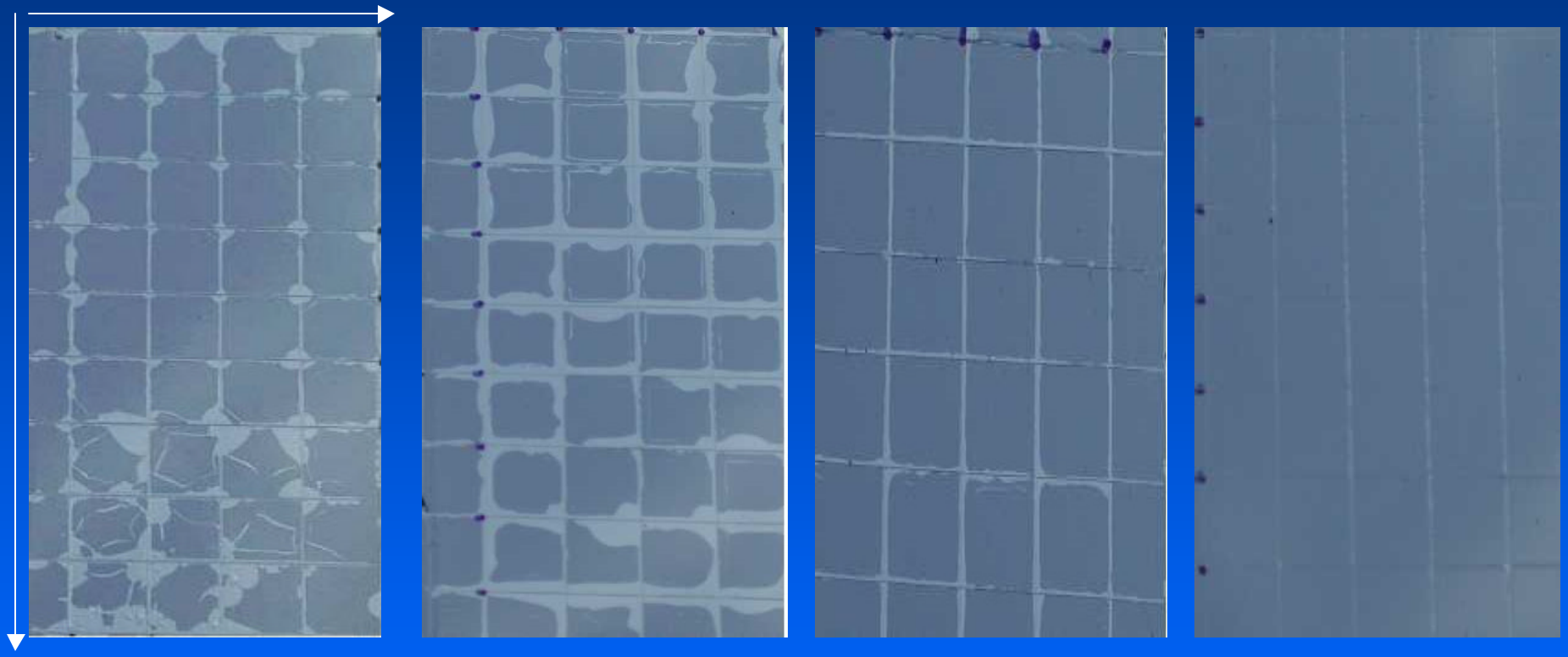


70°C for 64 h

140°C for 20 h

PMMA Film with Orthogonal Contact Angle and Thickness Gradients

(Annealed Below or Above its T_g)



70°C for 64 h, cut before

70°C for 64 h, cut after

140°C for 20 h, cut before

140°C for 20 h, cut after

=> Conclusion

- Above T_g annealing is more effective to enhance the adhesion
- No obvious thickness dependence on adhesion

Samples for Combi Peel off Test

Spin coating film (5wt.% chloroform solution)

→ Floated off on water surface →

Transferred on to the substrates Si (Al, Cu, Au, etc)

PMMA film thickness: **100-120** nm

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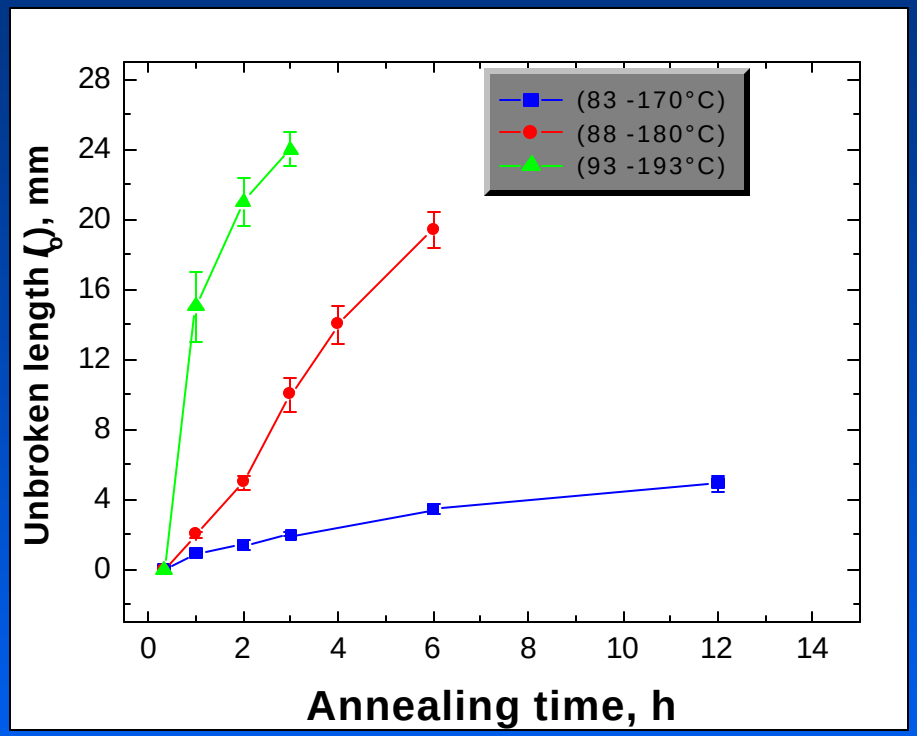
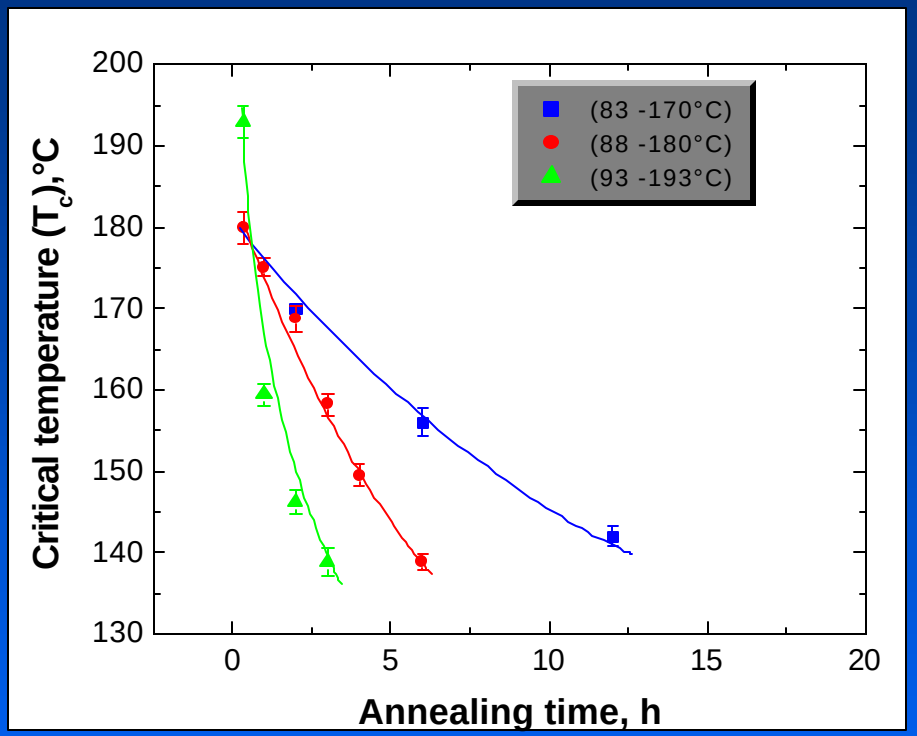
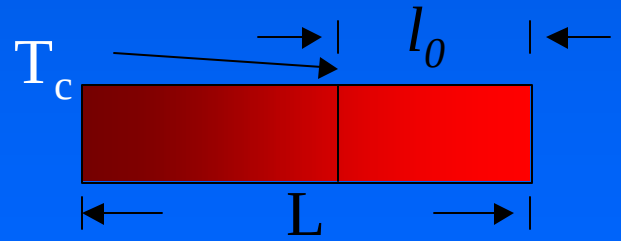
Adhesion of PMMA on Si

(Annealed on Thermal Gradient, then Peeled – Off)







l_0: unbroken length
T_c: critical temp.

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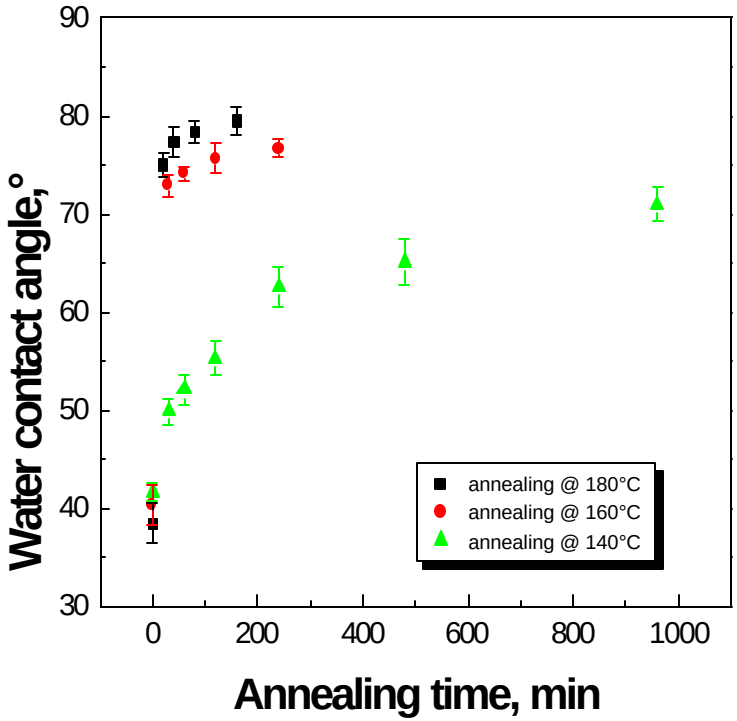
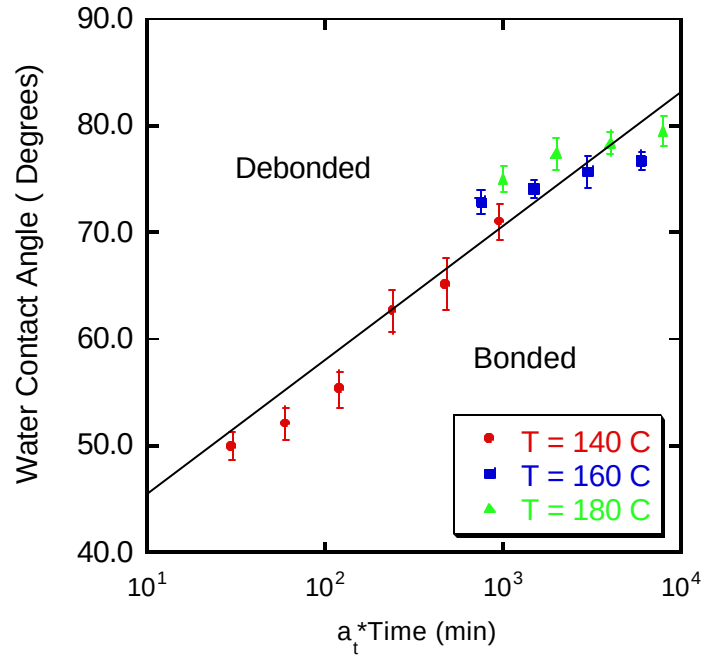
Adhesion of PMMA on Substrate with Contact Angle Gradient





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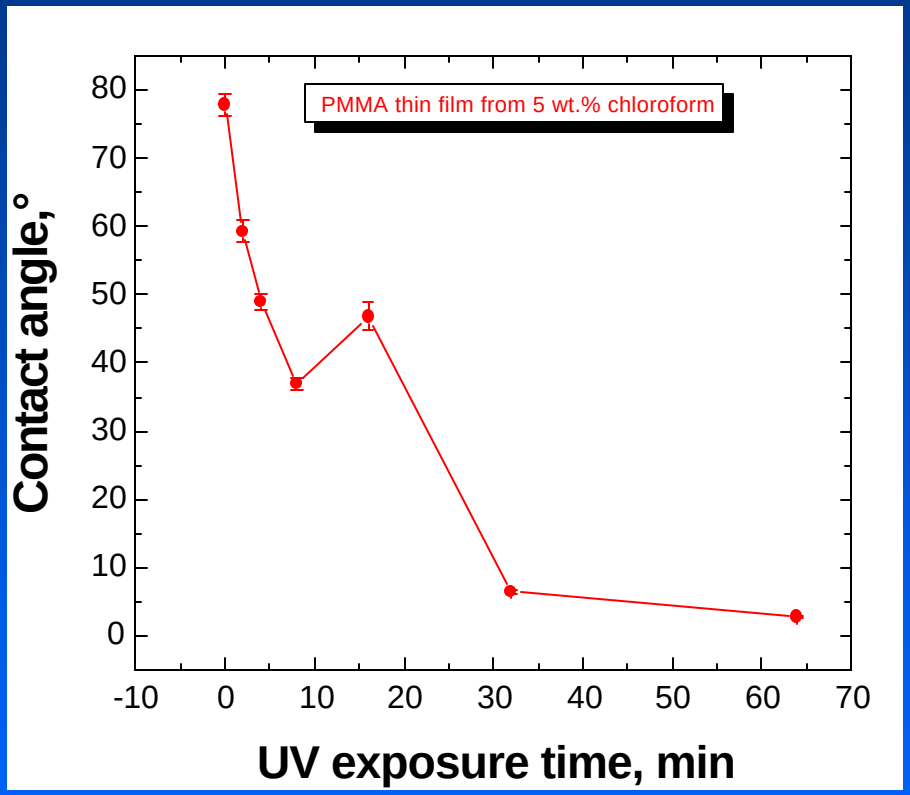
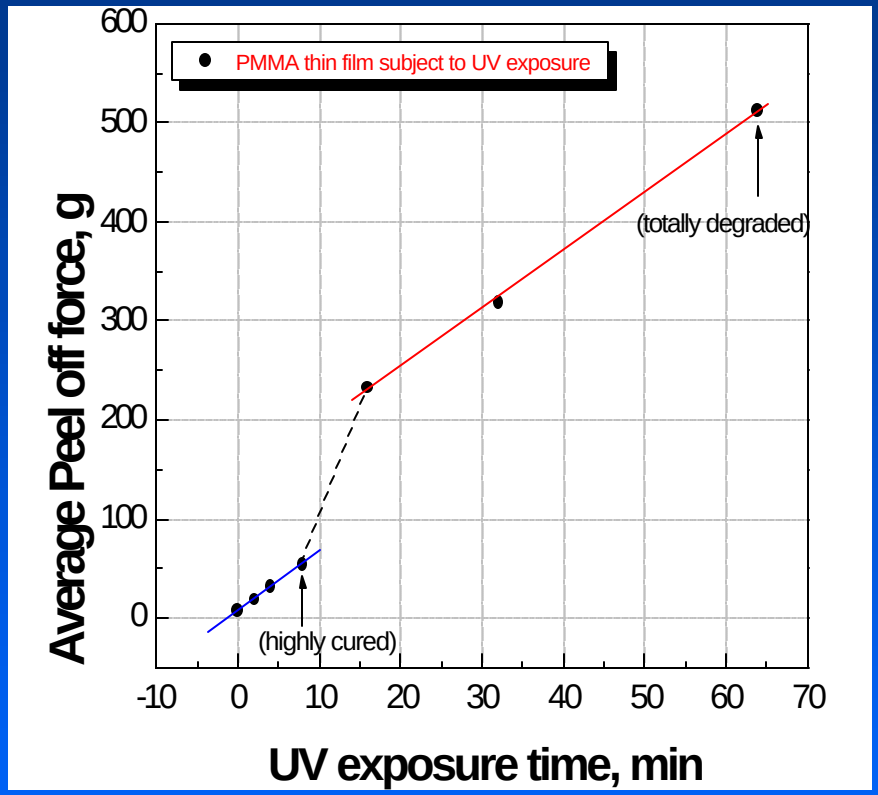
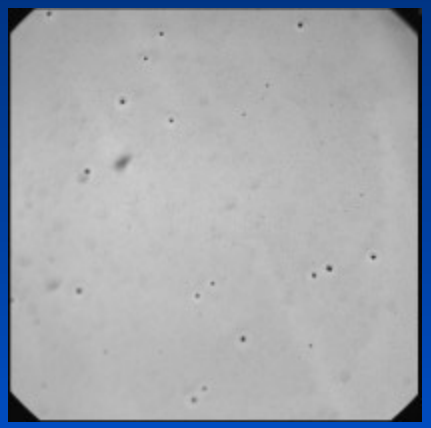
PMMA after UV Exposure Gradient - Contact Angle and Peel off Force





Effect of UV Exposure Time on PMMA Thin Film



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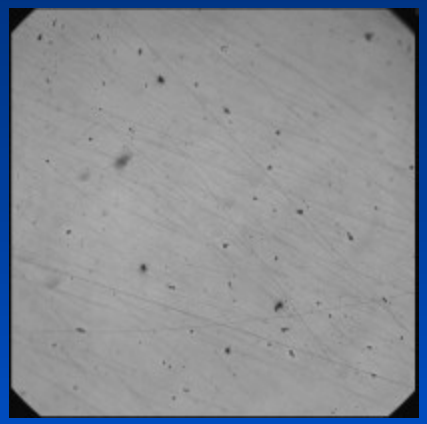

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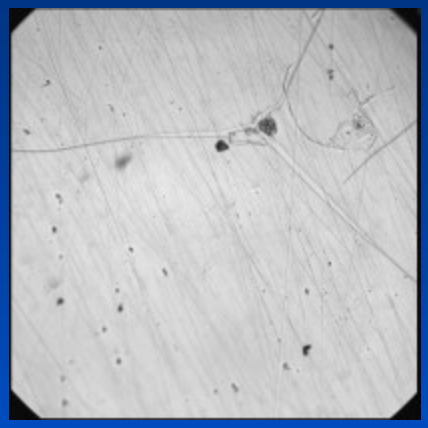
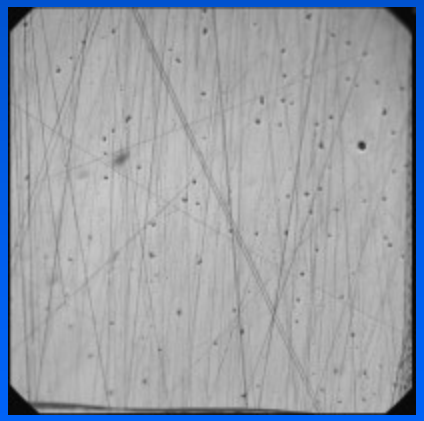


4 min



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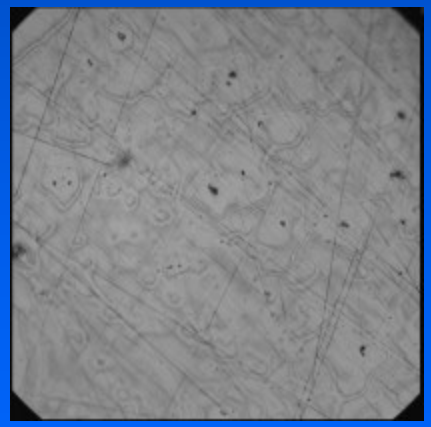

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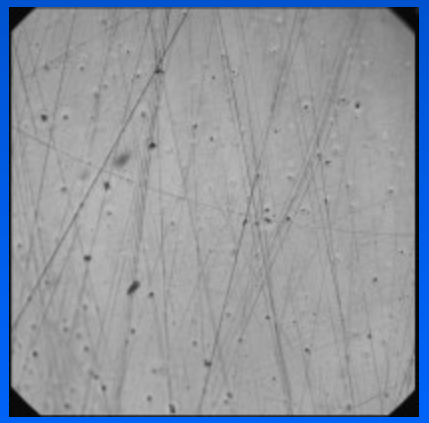

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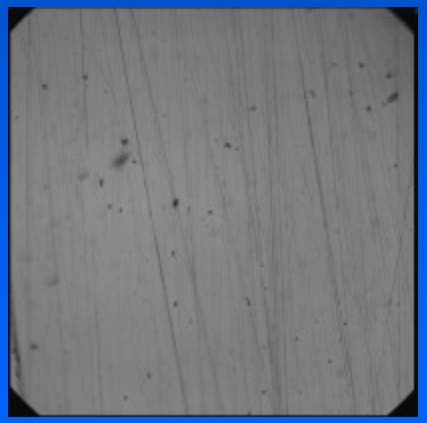

64 min

UV Effect of Exposure Time on PMMA Thin Film Surface

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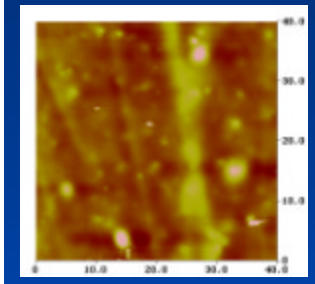
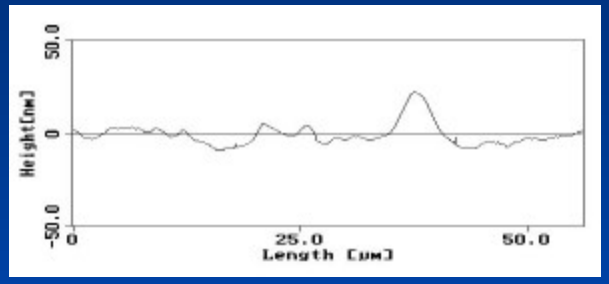

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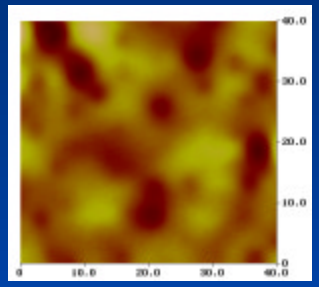
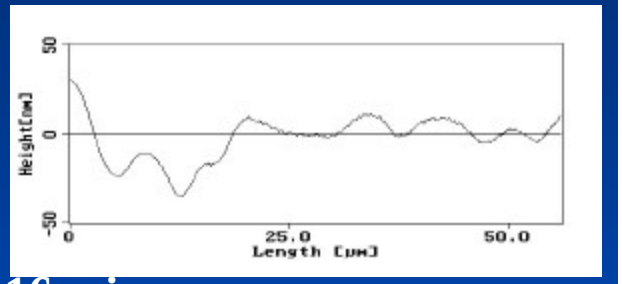

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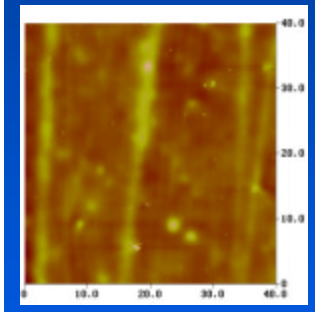
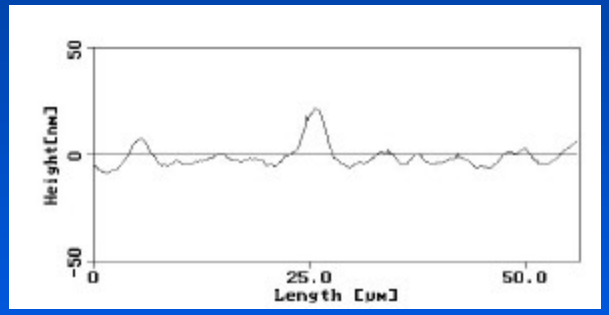

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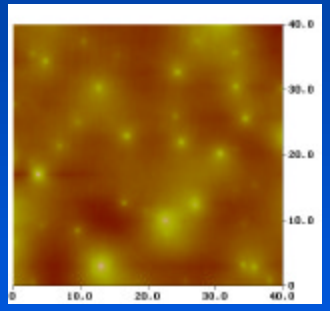
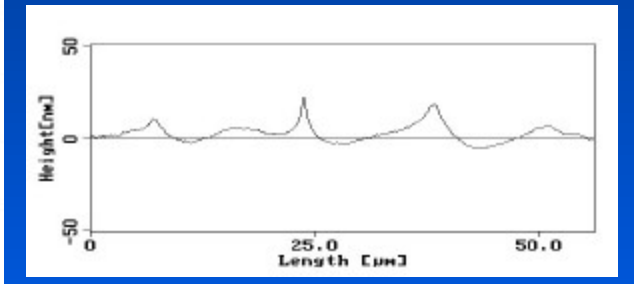

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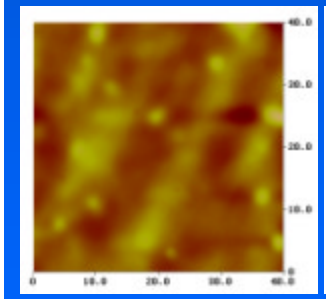
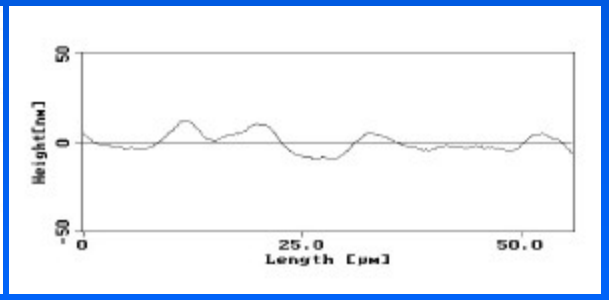

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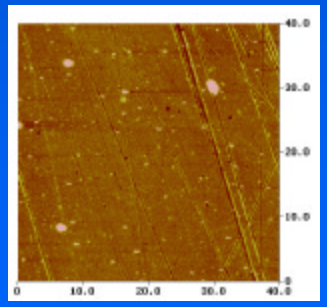
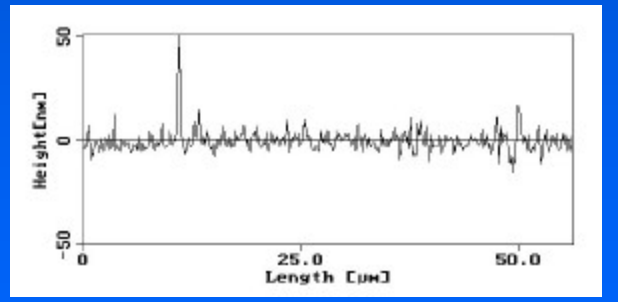
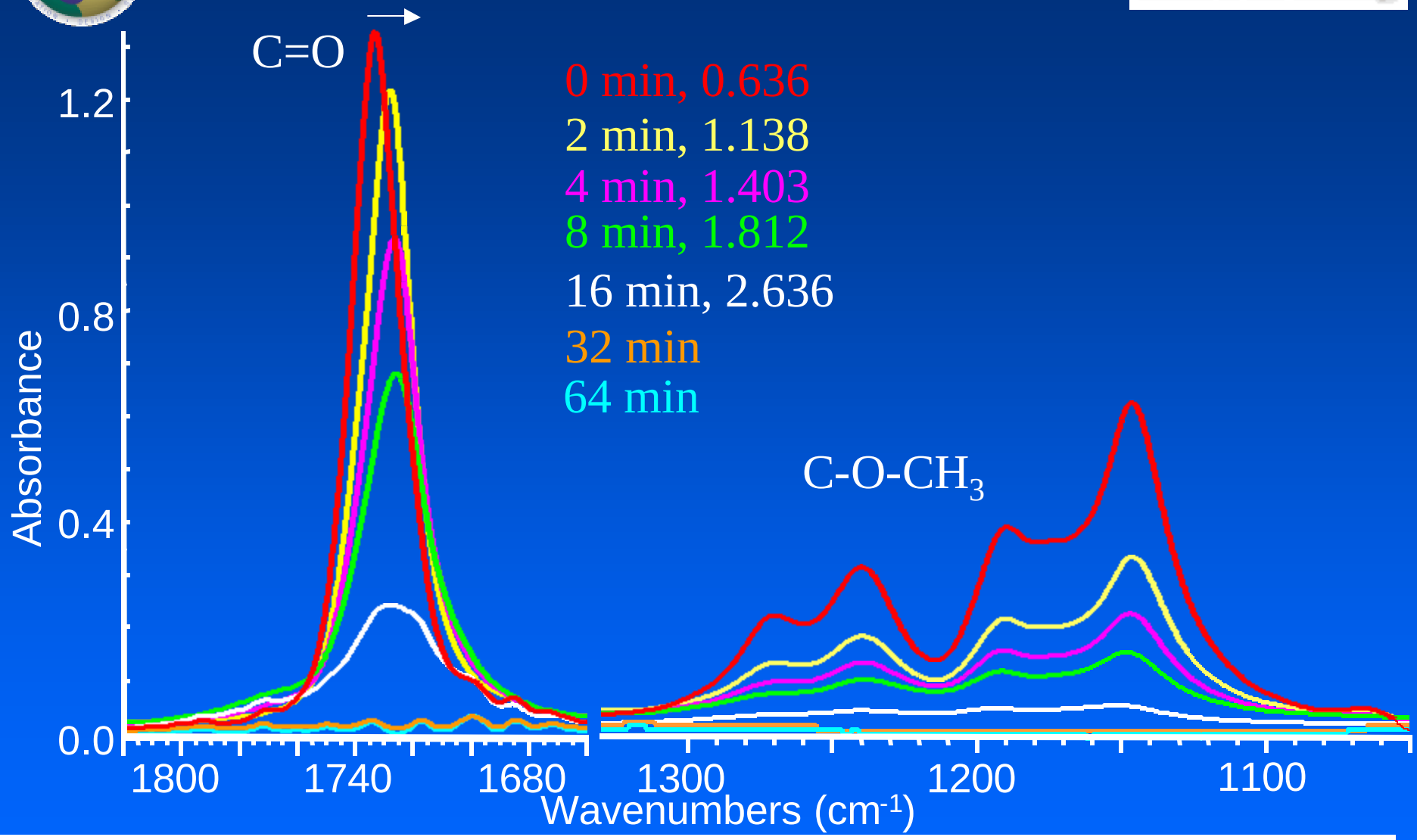



64 min

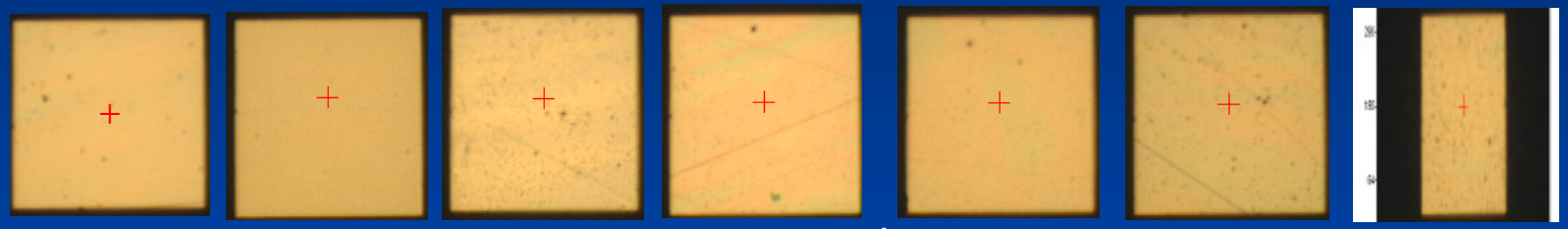
Roughness of PMMA film after UV Exposure

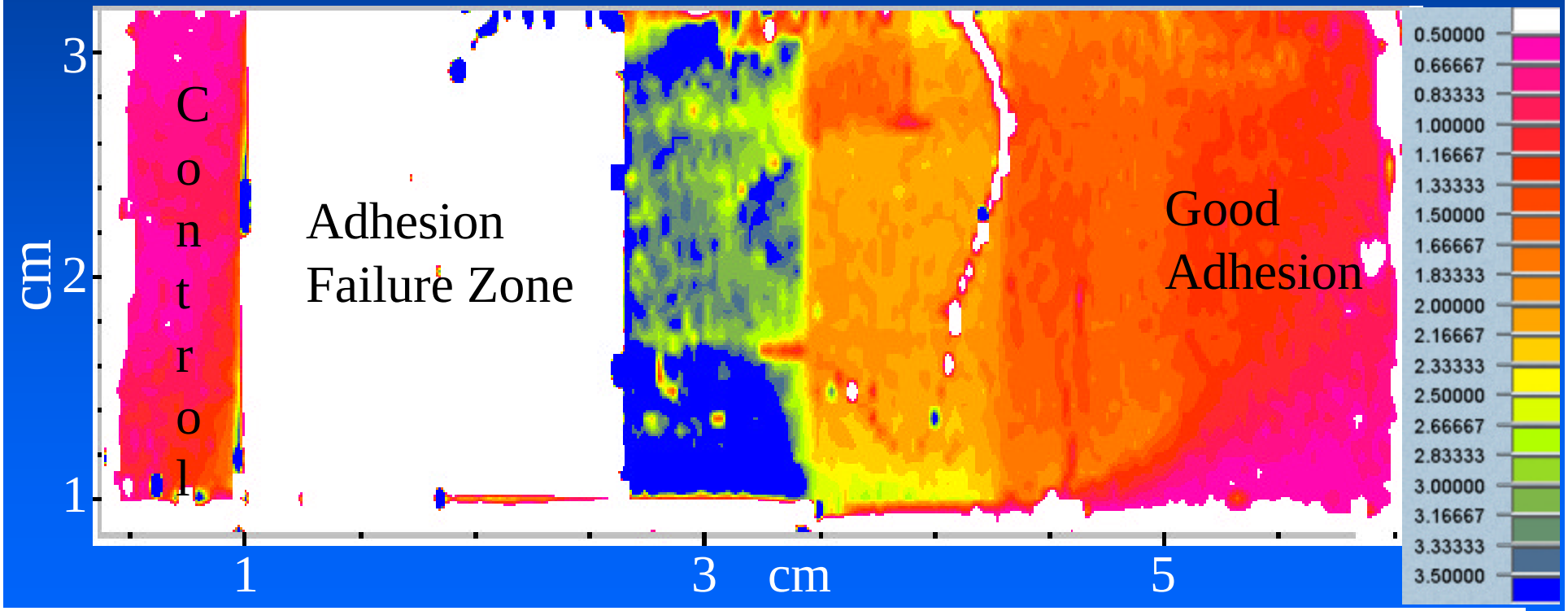
UV-O time, min	RMS, nm	R_a, nm
0	3.52	2.78
2	9.83	6.50
4	5.73	4.13
8	6.90	5.44
16	10.49	7.82
32	5.13	3.86
64	4.14	3.27

C=O / C-O-CH_3 Ratios



C=O / C-O-CH_3 FTIR Map





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Effect of Casting Solvent on PMMA Thin Film Adhesion

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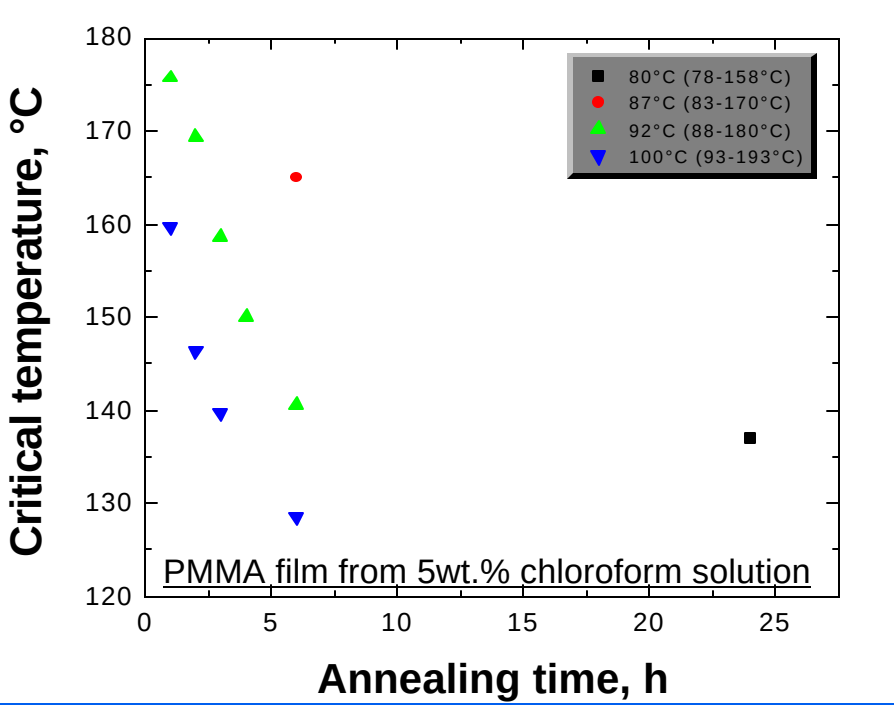
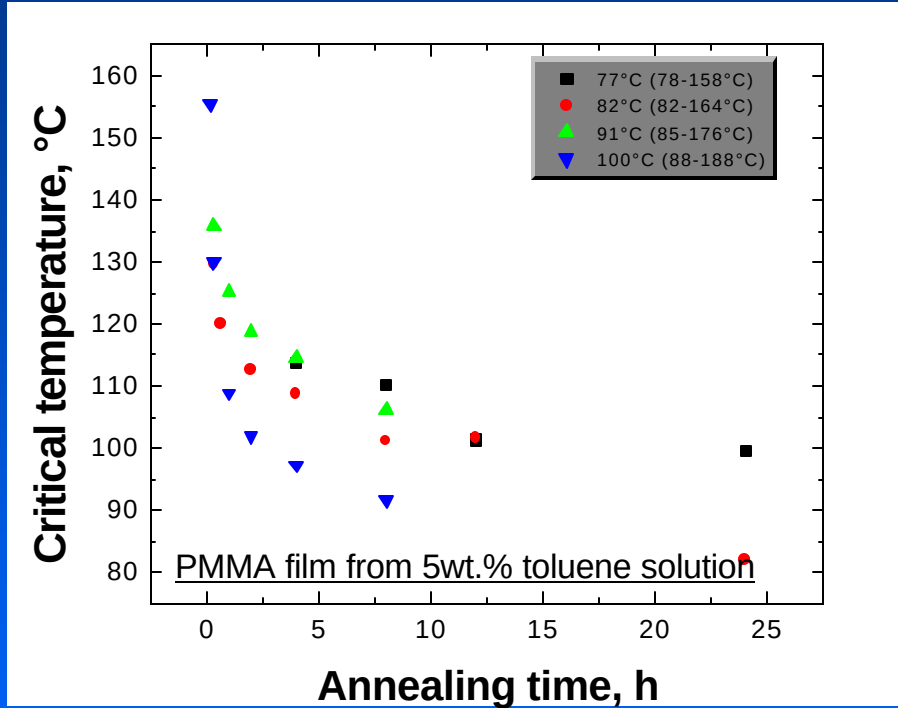
Chloroform



Toluene



Solubility Parameter:

PMMA: 22.7 $MPa^{1/2}$; Toluene: 18.2 $MPa^{1/2}$; Chloroform: 19.0 $MPa^{1/2}$.

Polymer Handbook, 4th edition, 1999, J. Brandrup; *et.al*

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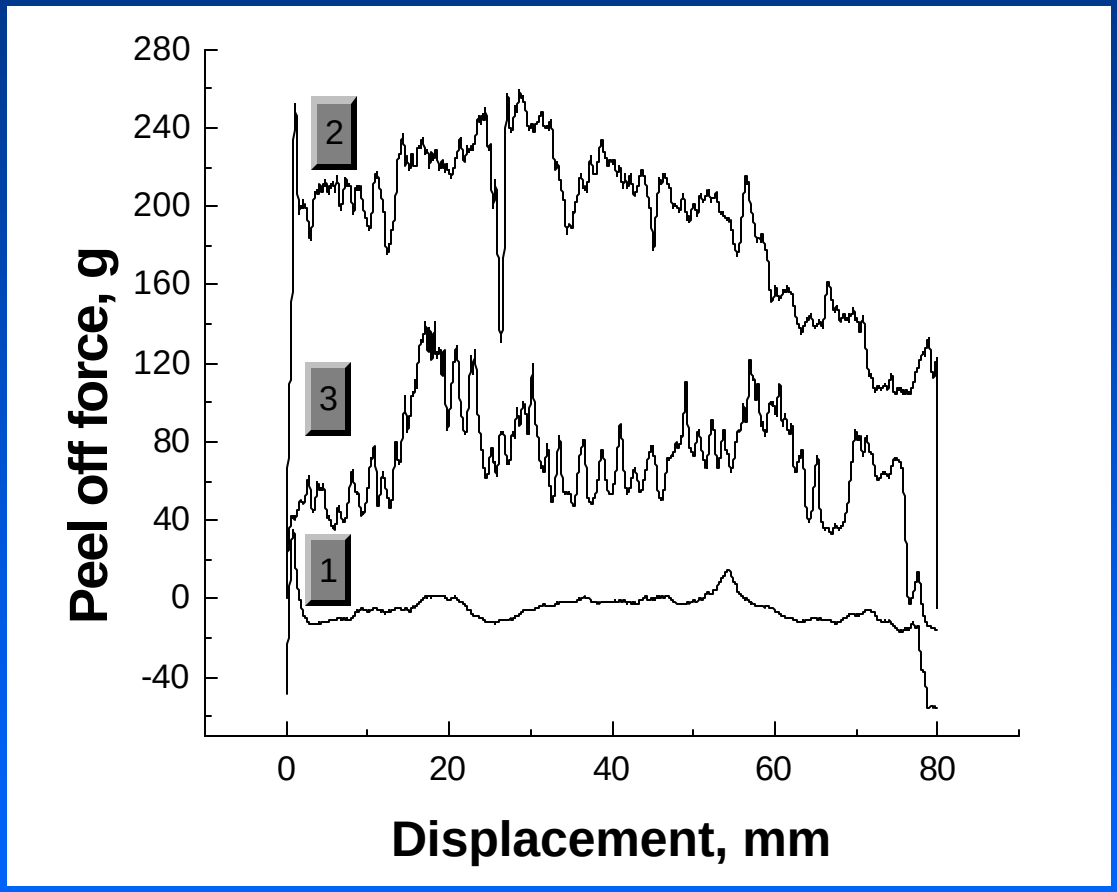
Tapes Used for Peel off Test

Different Tapes on the Highly Cured PMMA Thin Film



G_{IC}, (g/cm)

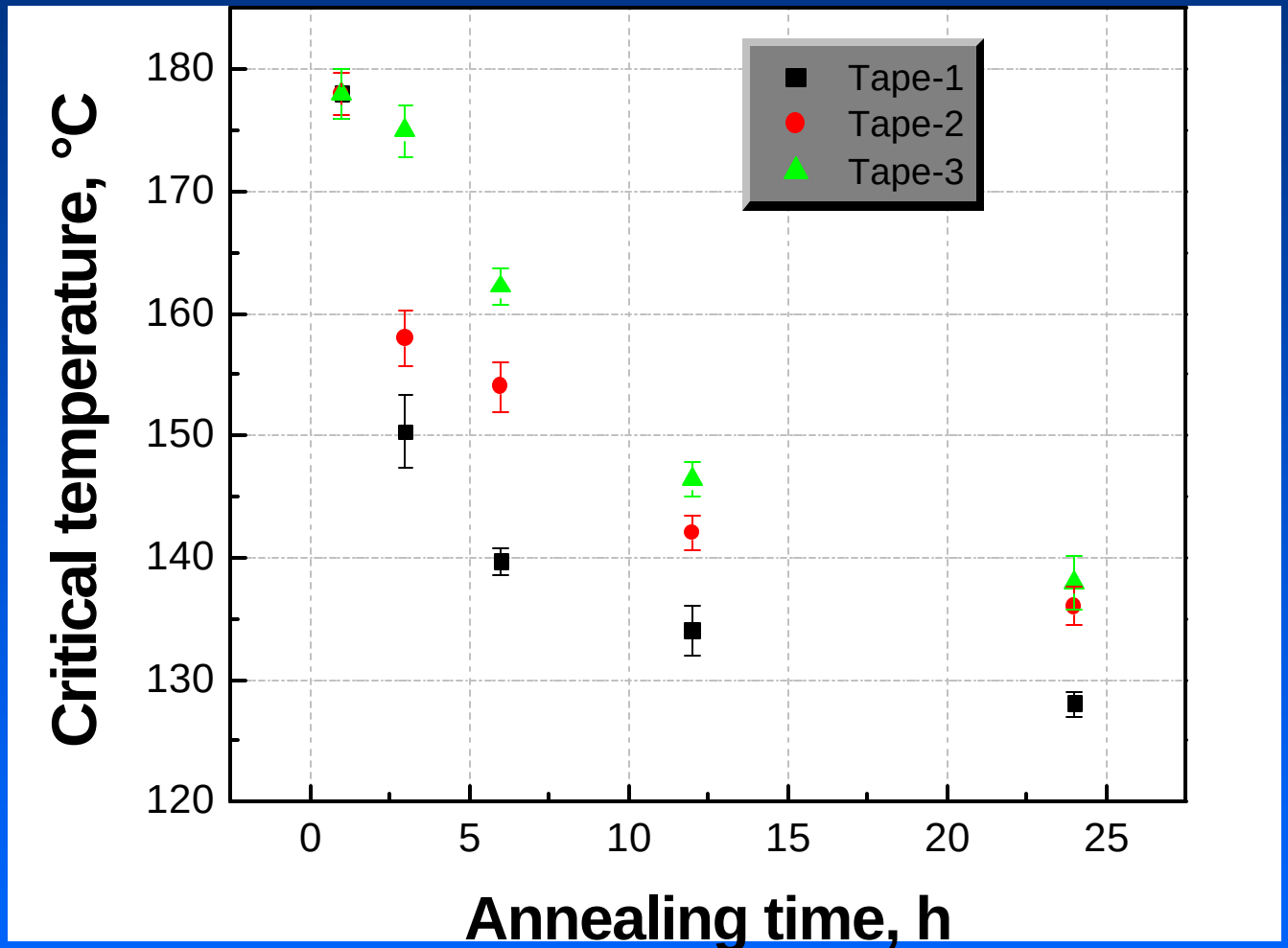
Tape 1: 43.92

Tape 2: 192.5

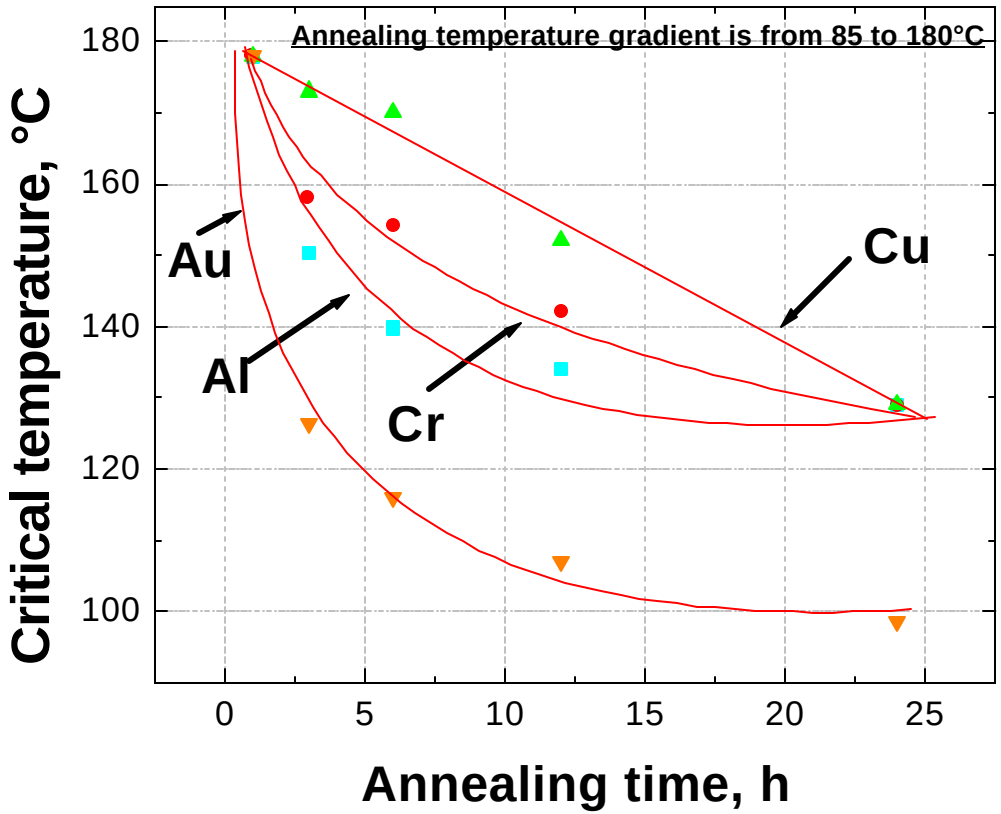
Tape 3: 94.2

Peel-off with 3 Different Tapes

(PMMA thin film annealed @85-178°C for different time)



Adhesion Behavior for PMMA on Different Metals- Al, Cr, Cu and Au



Outline

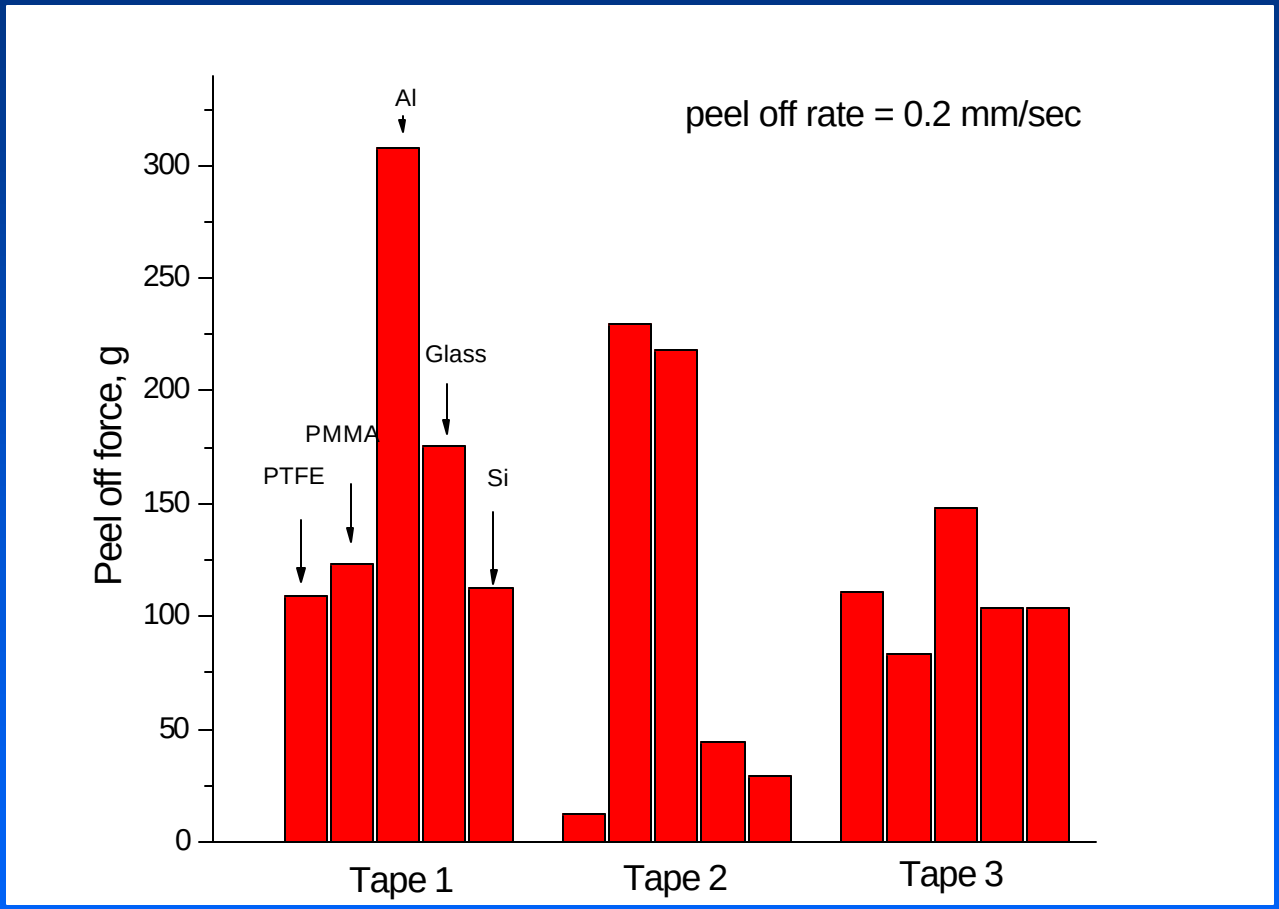
Methods

Polymer Debonding
Peel-off Test

Test Systems

Stress gradient on PMMA adhesion
Surface energy gradient on PMMA adhesion
Temperature effects on adhesion
Gradient UV-exposure on PMMA stability
Casting-solvent effect on PMMA adhesion
Material aspects (different tapes, metals)
→ *Tape adhesion on surface energy gradient*

Adhesion Dependence on Surface Energy of Substrate Materials

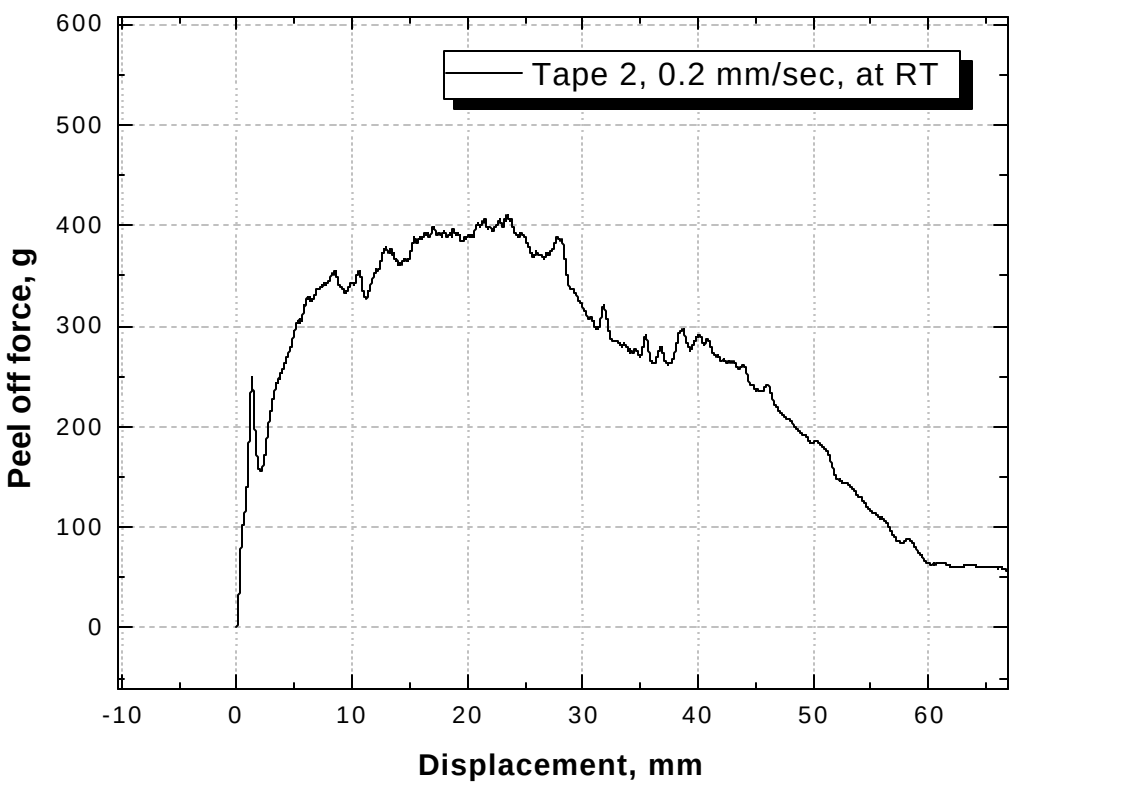


Details of Some Substances

	θ_{H2O}	θ_{CH2I2}	γ_{sp}	γ_{sd}	γ	Polarity
PTFE	135.2	83.99	1.81	18.68	20.49	0.088
PMMA	79.88	52.23	6.27	28.47	34.74	0.180
Al	59.06	34.52	15.43	33.61	49.03	0.315
Glass	11.42	60.52	58.06	14.31	72.37	0.802
Silicon	0	45.01	50.98	21.82	72.80	0.700

Note: Al was baked at 450°C 8-12 h; the CA for newly prepared Al was ca. 47°;
PMMA was spin coating on Si wafer from 5 wt.% chloroform solution, 1500 rpm;
Glass was sonicated in toluene for 10 min;
Silicon was UV burned for 20 min, then rinsed by DI water and dried with N_2.

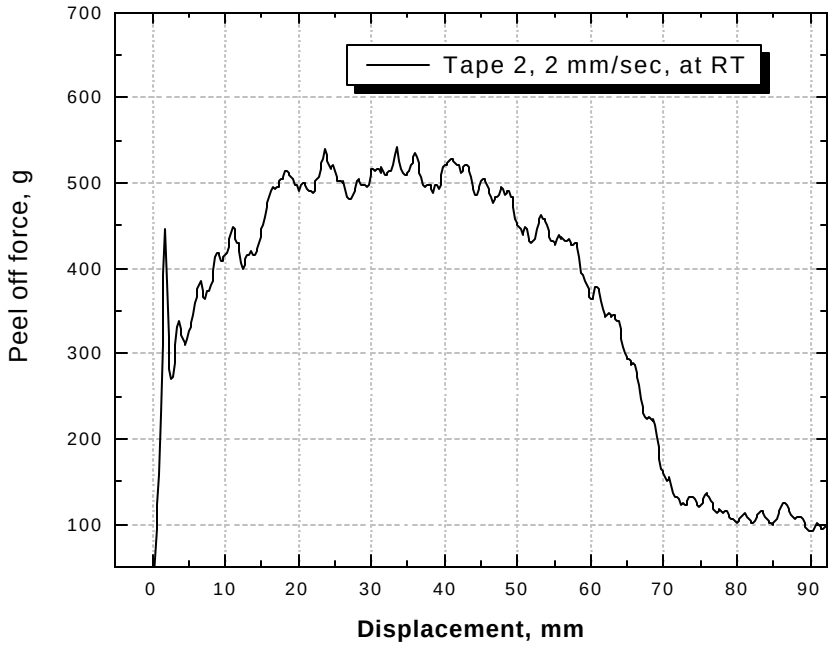
Peel off on Surface Energy Gradient Surface

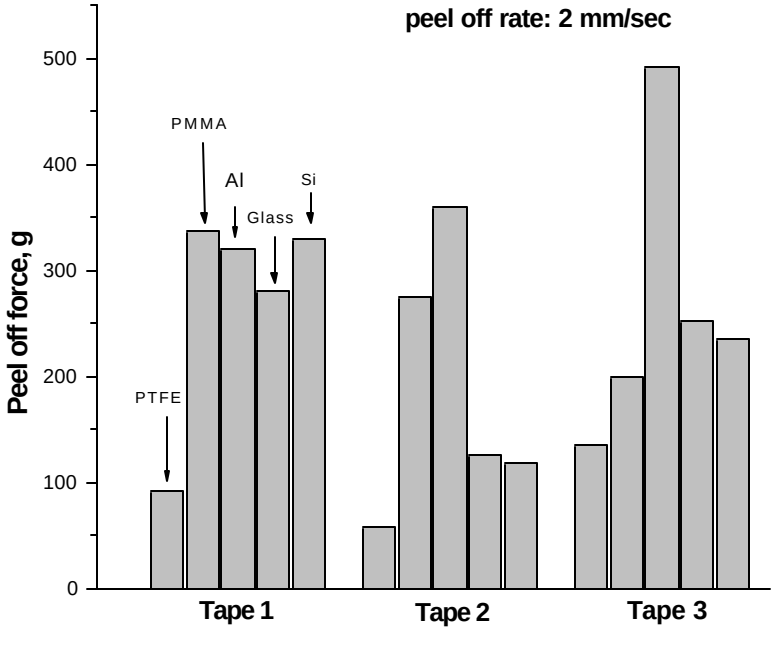


~30 ⟷ ~50

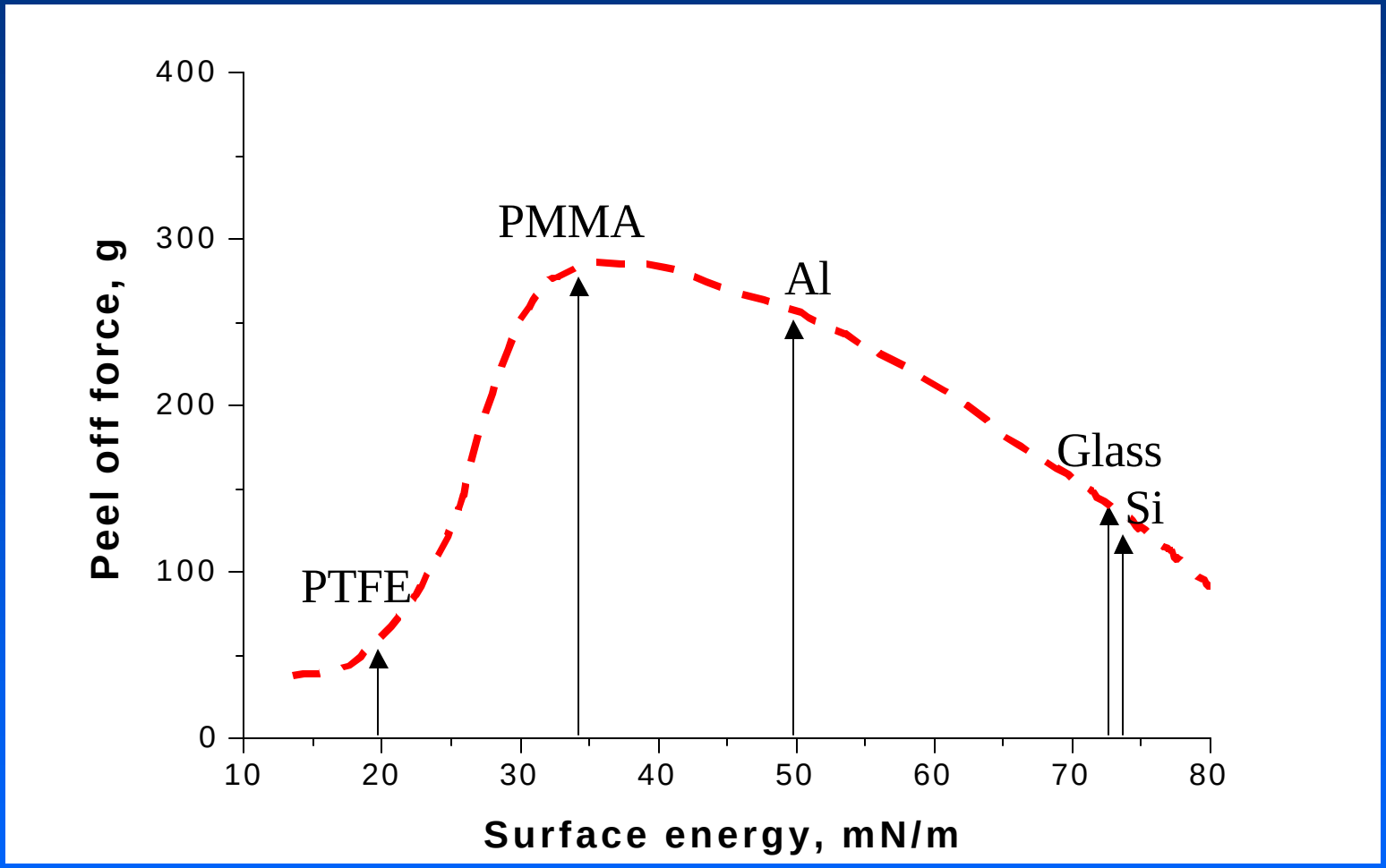
Surface Energy(mN/m)

Adhesion Dependence on Surface Energy of Substrate Materials





Peel off Force vs. Surface Energy



Future directions

- Investigate substrate roughness effects
- Investigate adhesion of photo-resists before /after cure and rinse cycle
- Investigate multi variable behavior in one experiment
- Microlens experiments to quantify the adhesion and relaxation
- Correlate Peel-tests with Microlens tests
- Measure temperature gradients effects on-line in Peel Tests

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