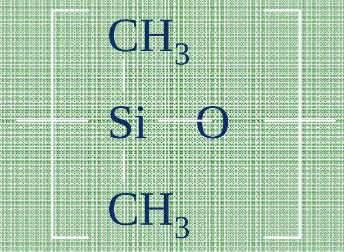
Surface modification of polymer : PDMS *(Poly-dimethylsiloxane)*

PDMS(poly-dimethylsiloxane)?

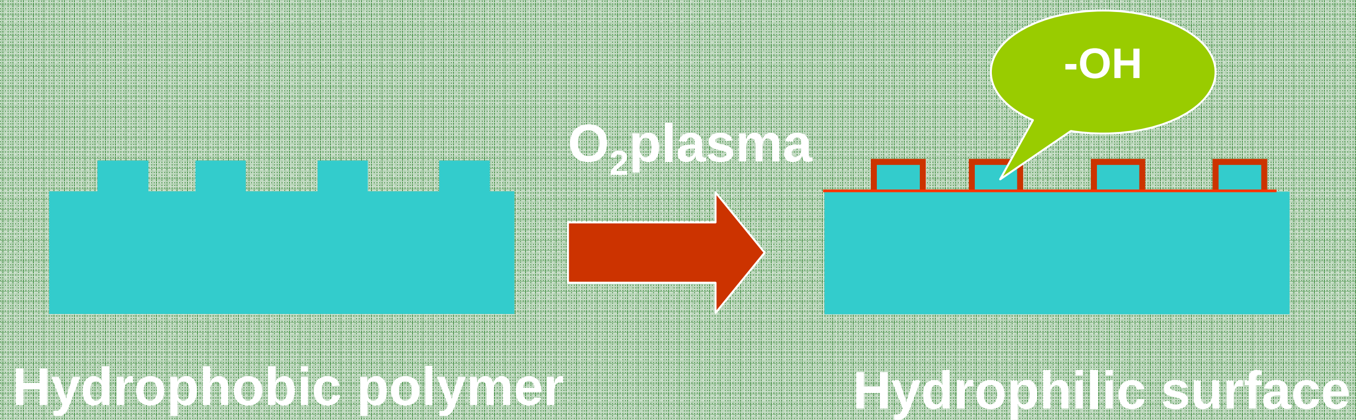


- Applicatons: Soft lithography
  - Bio sensor by microcontact printing
  - Micromolding
  - Micro Transfer molding & Decal transfer molding

    Microfludics
  - Lab on a Chip
  - U-TAS

Advantages &	Disadvantages
Isotropic and homogeneous	Extremely hydrophobic
Chemically inert	Strong tendency to adsorb other molecules onto the surface
Optically transparent	Unstable and poorly controlled electroosmotic flow
Good thermal stability	
Easily and inexpensively fabricated	

소수성-친수성

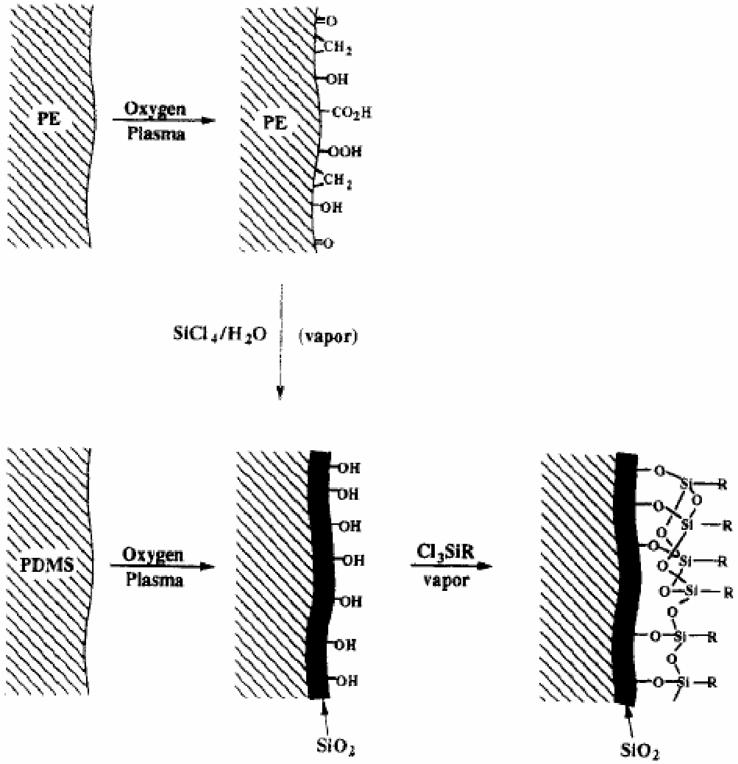


Monolayers on Disordered Substrates: Self-Assembly of Alkyltrichlorosilanes on Surface-Modified Polyethylene and Poly(dimethylsiloxane)

Macromolecules 1993, *26*, 5870–5875

Gregory S. Ferguson,[1a] Manoj K. Chaudhury,[1b] Hans A. Biebuyck, and George M. Whitesides*

Scheme I. Schematic Illustration of the Synthesis of SAMs on PE[ox]/SiO_2 and PDMS[ox][a]



[a] The thickness of the surface film of SiO_2 on polyethylene is probably between 200 and 1000 Å, depending on the number of treatments with $SiCl_4$ (see Experimental Section) and is not drawn to scale.[14] The thickness of the silicate layer on PDMS[ox] is less than 50 Å.[5]

Table I. Advancing (θ_a) and Receding (θ_r) Contact Angles on Hydrocarbon Surfaces[a,b]

material	water θ_a	water θ_r	hexadecane θ_a	hexadecane θ_r
PE[ox]/SiO_2/$O_3Si(CH_2)_{10}CH_3$	113	104	48	40
PE[ox]/SiO_2/$O_3Si(CH_2)_9CH{=}CH_2$	106	100	38	31
PDMS[ox]/$O_3Si(CH_2)_{10}CH_3$	112	103	46	45
PDMS[ox]/$O_3Si(CH_2)_9CH{=}CH_2$	104	99	36	35
Si/SiO_2/$O_3Si(CH_2)_{10}CH_3$	112	102	41	39
Si/SiO_2/$O_3Si(CH_2)_9CH{=}CH_2$	101	92	30	24
Au/$S(CH_2)_{10}CH_3$	115	105	48	42
Au/$S(CH_2)_9CH{=}CH_2$	107	97	39	33
PE-$CO_2(CH_2)_{11}CH_3$	125	≈40	wets	

Dynamics of Polymeric Solid Surfaces Treated with Oxygen Plasma: Effect of Aging Media after Plasma Treatment

JOURNAL OF COLLOID AND INTERFACE SCIENCE **202**, 37–44 (1998)

Estimation of Work of Adhesion and Surface Free Energy

Young–Dupre´ equation

$$W_A = \gamma_L(1 + \cos\theta)$$

W_A represents the quantity of polar functional groups on the surface treated by oxygen plasma.

where W_A is the work of adhesion (mJ/m^2), γ_L is the surface free energy of liquid (mJ/m^2), and θ is the contact angle (°).

Extended Fowkes equations

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_S^d\gamma_L^d} + 2\sqrt{\gamma_S^p\gamma_L^p} + 2\sqrt{\gamma_S^h\gamma_L^h}$$

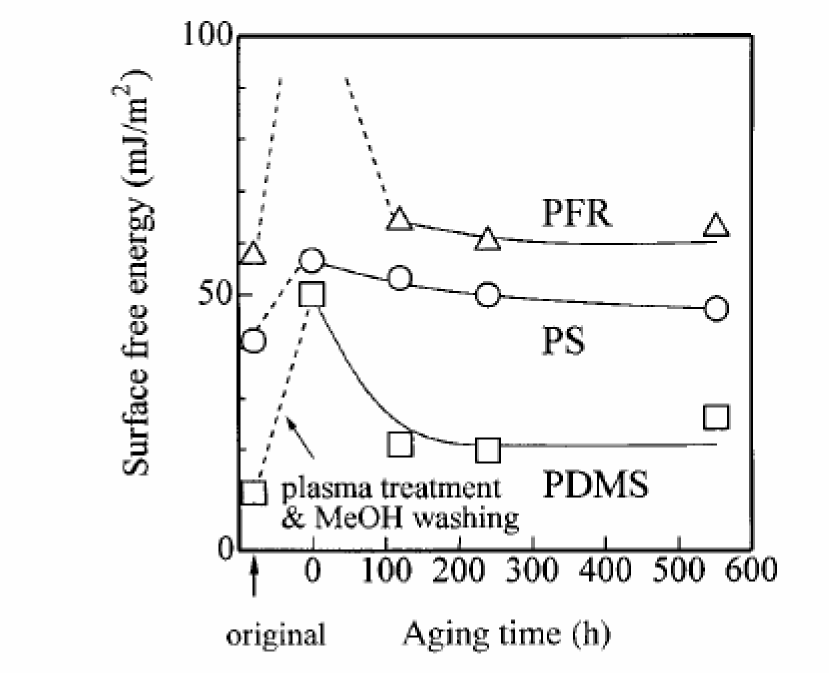
$$\gamma^{tot} = \gamma^d + \gamma^p + \gamma^h,$$

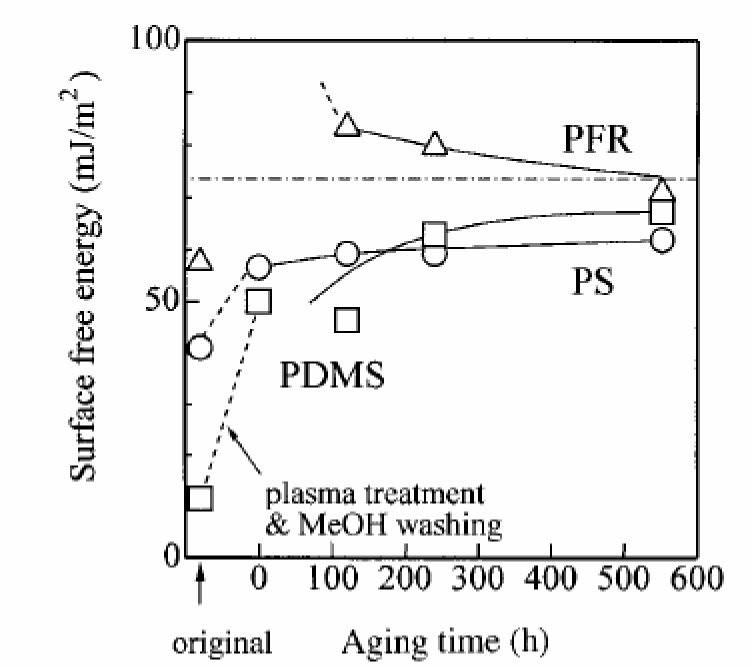
γ_S is the surface free energy of solid (mJ/m^2)

d is the dispersion force component
p is the polar component
h is the hydrogen bonding component of surface free energy,
tot is the total surface free energy

Contact Angles and Oxygen Concentrations on Polymer Surfaces

	Untreated		O_2 plasma-treated		Washed with methanol[a]	
Polymer	Contact angle (°)[b]	Oxygen (at.%)[c]	Contact angle (°)	Oxygen (at.%)	Contact angle (°)	Oxygen (at.%)
PS	91.6	0.5	6.9	19.3	63.9	14.4
PFR	62.4	20.2	11.2	38.7	8.5	36.5
PDMS	109.9	30.8	8.4	53.5	69.0	39.8





In Nitrogen

In Water

-For PS & PDMS, washing with methanol after plasma treatment led to a decrease in surface oxygen concentrations: the low-molecular-weight oxidation products were removed from the polymer surface.
-T_g of PDMS is below RT and the mobility of the molecular chain is high.
-In water, the oxygen-containing polar functional groups in the surface layers of the films were thought to orient toward the topmost surfaces.

Summary of Surface Free Energies

Polymer	γ_P (mJ/m^2)[a]	γ_T (mJ/m^2)[b]
PS	40	57
PDMS	10	50
PFR	58	>100

Medium	γ_M (mJ/m^2)[c]
Water	72.8
Nitrogen	~0

[a] γ_P, the surface free energy of the untreated polymer film.
[b] γ_T, the surface free energy of the O_2-plasma-treated layer.
[c] γ_M, the surface free energy of the aging medium.

The interface free energy: A-B

$\gamma_{AB} = (\sqrt{\gamma_A} - \sqrt{\gamma_B})^2$

- 1. $\gamma_T > \gamma_P > \gamma_M$ 일 때, $(\sqrt{\gamma_T} - \sqrt{\gamma_M})^2 > (\sqrt{\gamma_P} - \sqrt{\gamma_M})^2$

  이럴경우, 소수성의 untreated polymer film 이 열역학적으로 medium과 친하게 된다. 따라서 친수성의 표면 물질들은 안으로 향하고 소수성의 고분자 내부 물질이 밖으로 나와서 표면이 다시 소수성으로 바뀐다. (In nitrogen 폴리머 aging)

- 2. $\gamma_M > \gamma_T > \gamma_P$ 일 때, $(\sqrt{\gamma_T} - \sqrt{\gamma_M})^2 < (\sqrt{\gamma_P} - \sqrt{\gamma_M})^2$

  이럴경우, polar functional group이 표면 쪽으로 orient 되어서 더욱 안정화 하려고 한다.(물속에서 PS와 PDMS를 aging 했을 경우와 일치)

- 3. $\gamma_T > \gamma_M > \gamma_P$ 일 때, 이때는 각 변수의 크기에 따라 다르다.

  물속에서 PFR을 aging 할경우 1번과 같게 되어 표면 물질이 오히려 bulk 쪽으로 향하게 된다.

PDMS in Microfluidic Devices

Microfluidics is the handling and dealing with small quantities of fluids.

- ✓ PDMS-based microfluidic devices are increasing in popularity due to their ease of fabrication and low costs.
- ✓ Despite this, there is a tremendous need for strategies to rapidly and easily tailor the surface properties of these devices.

Why Microfludics?

- Minimize physical size and space
- Low power and low production cost per device
- Efficient use of reagents and reactants
- Fast response time
- Precise volumetric control
- Utilize microfluidic phenomena

Surface Modification Methods of PDMS

- Oxygen plasma treatment
  - Duffy and Whitesides, 1998
  - Gregory and Michael, 1998
- Silanization
  - Grzybowski and Whitesides, 1998
- Adsorbed coating (Polybrene/dextransulfate)
  - Barker and Locascio, 2000
  - Liu and Henry, 2000
- Protein or lipid coating
  - Linder and Sigrist, 2001

✓ Unstable requirging periodic reapplication

✓ Ill-defined and heterogeneous surface properties

✓ Difficult multistep procedures

✓ Undesirable buffer solution

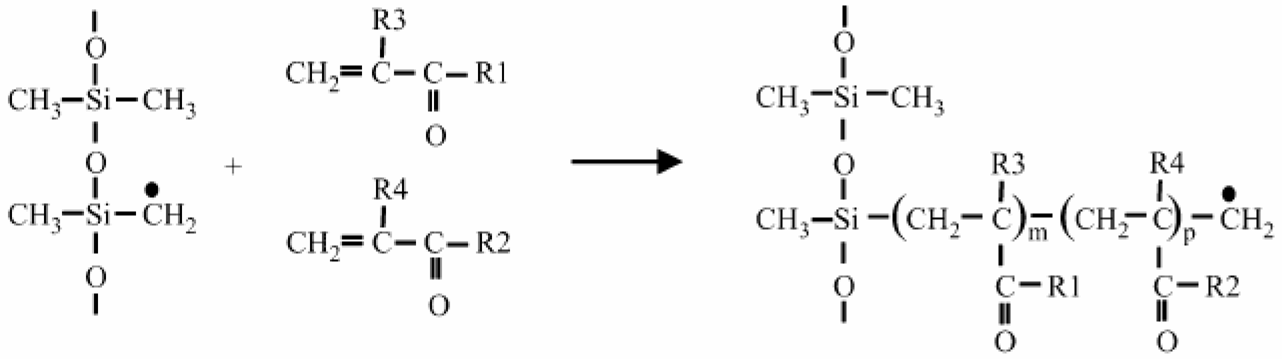
- Ultraviolet polymer grafting
  - Shuwen and Allbritton, 2002

Covalently attached coatings with selectable surface properties

Tailoring the Surface Properties of Poly(dimethylsiloxane) Microfluidic Devices

Shuwen Hu,[†] Xueqin Ren,[†] Mark Bachman,[‡,§] Christopher E. Sims,[||]
G. P. Li,[*,†,§,‡] and Nancy L. Allbritton[*,†,||]

Langmuir 2004

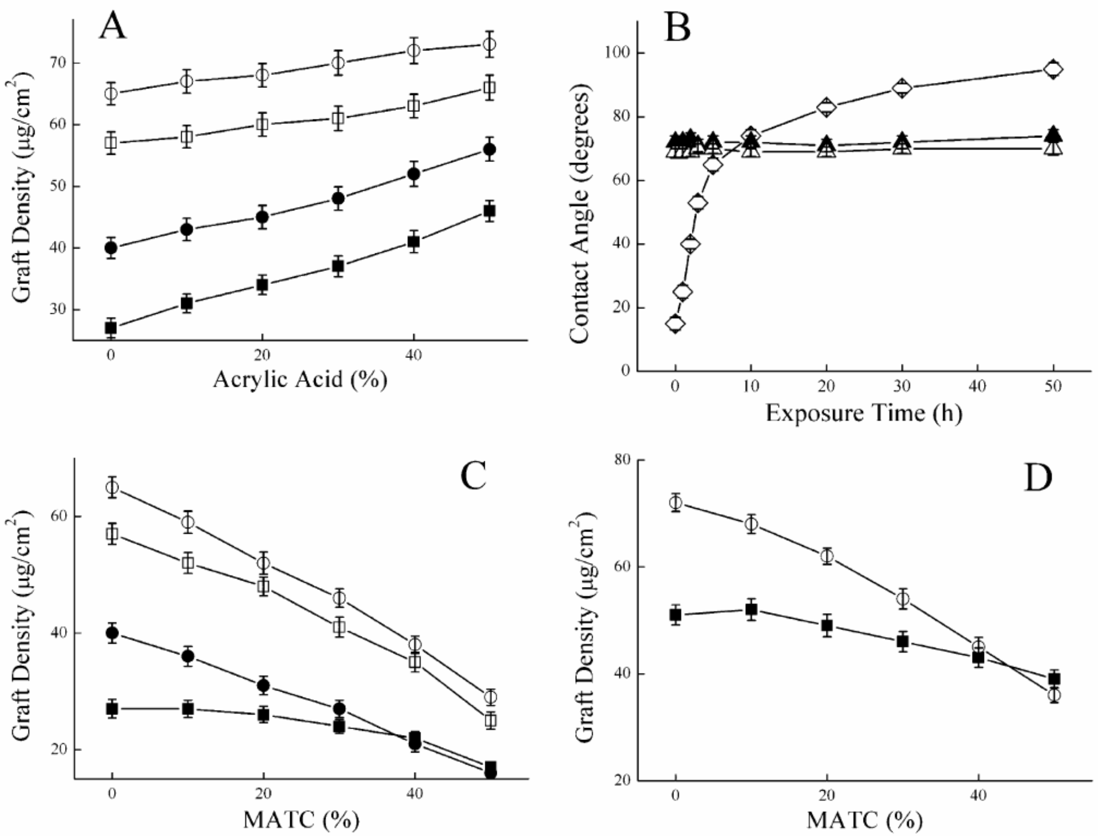


R1,R2:	$-$ OH	acrylic acid (AA)
	$-$ NH_2	acrylamide (AM)
	$-$ $N(CH_3)_2$	N,N-dimethylacrylamide (DMA)
	$-$ OCH_2CH_2OH	2-hydroxyethyl acrylate (HEA)
	$-$ $O(CH_2CH_2O)_nCH_3$	poly(ethylene glycol) monomethoxy acrylate (PEG)
	$-$ $OCH_2CH_2N(CH_3)^+Cl_3^-$	(2-methacryloxyethyl)trimethylammonium chloride (MATC)

R3,R4:	$-$ H	AA, AM, DMA, HEA, PEG
	$-$ CH_3	MATC

Table 1. Contact Angles of Devices Grafted with Co-Mixed Monomers[a]

mixture	ratio (w/w)	graft density[b] ($\mu g/cm^3$)	contact angle[b] (deg)
HEA/AA	10:1	58 ± 2	52 ± 1
AM/AA	10:1	67 ± 2	61 ± 1
DMA/AA	10:1	43 ± 2	75 ± 2
PEG/AA	10:1	29 ± 1	75 ± 2
HEA/MATC	10:1	52 ± 2	55 ± 1
AM/MATC	10:1	59 ± 2	63 ± 1
DMA/MATC	10:1	36 ± 2	77 ± 2
PEG/MATC	10:1	27 ± 1	77 ± 2
native PDMS			109[c]
oxidized PDMS			15[c]



요약

1. Polymer 표면을 modification 하기 위해서는 먼저 표면 activation 시켜야 한다.
   -산소 플라즈마, UV, 산처리 방법등이 가능

2. 보관하는 방법에(Medium) 따라서 표면성질이 회복 혹은 가역적으로 조절이 가능하다. 따라서 보관할때 조건에 주의하여야 한다. 그렇지 않을 경우 표면처리를 한 후 될수 있는대로 곧바로 실험을 한다.