「膜工学春季講演会」膜工学サロン（ZOOM）
2022/3/29
サロン D(16:10~17:50)

量子ビームから捉える薄膜・界面の相互作用

神戸大学　大学院　工学研究科
松本　拓也

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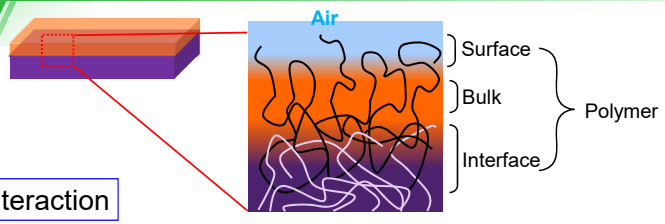
Surface and Interface of Polymers



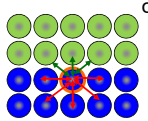
Interaction

Bulk ····**Polymer chain** VS Polymer chain　Stable

Surface ····**Polymer chain** VS Air (or none)　Unstable

Interface ····**Polymer chain** VS **Other polymer chain** or **Solvents**　Unstable

Mobility Up or Down
T_g Up or Down



Asymmetric chemical interaction
+ physical factor

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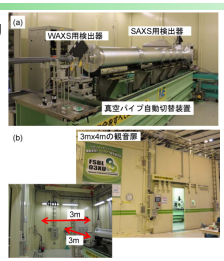
Synchrotron Radiation

• **X-ray beam**

http://www.spring8.or.jp/e/

BL03XU



• Beam Intensity : 100,000,000 times (vs X-ray beam @Lab.)
• Beam Divergence : 0.00086°（0.01°　@Lab.)

• One measurement : < 1sec (30 min @Lab.)

➡ *in situ* or *operand* measurements

• SAXS, WAXD, XAFS, IR, CT,,,, etc.

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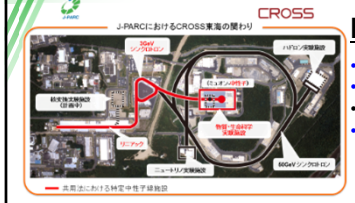
Synchrotron Radiation

• **Neutron beam**　J-PARC　MLF@Tokai



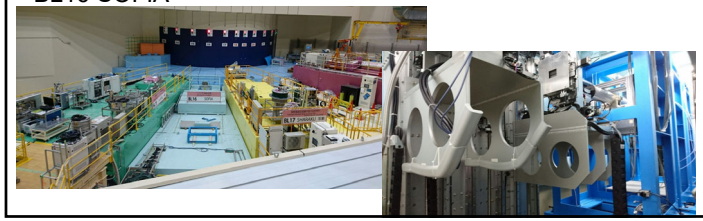
Neutron beam

- no electric charge
- distinguish isotopes (nucleus)
- sensitive to atomic and molecular structure
- high transmittance

• detect hydrogen and deuterium
Polymer VS water

X-ray beam
- detect the difference of densities

BL16 SOFIA



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Outlines

1. 水をはじく高分子とはじかない高分子の界面

2. 水を吸う高分子の内部構造

3. 高分子の接着界面に発生する応力

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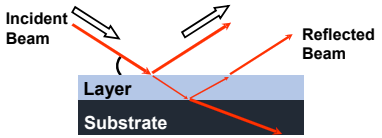
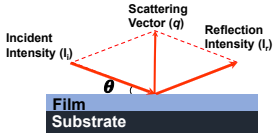
Neutron Reflectivity (NR)

Interference of light
+
Neutron beam



Scattering vector : $q = 4\pi\sin\theta/\lambda$



Reflectivity : $R(q) = I_r/I_i$

Bragg's Law : $n\lambda = 2d\sin\theta$

Scattering length density (SLD)

$$\rho = \frac{N_A \rho_{mass}}{M_w} \sum_{aroms} b_c$$

For example,,,

$\rho(H_2O) = -0.22\times10^{-4}$ nm^{-2}
$\rho(D_2O) = 6.33\times10^{-4}$ nm^{-2}
ρ(polymer) = 1~2 × 10^{-4} nm^{-2}

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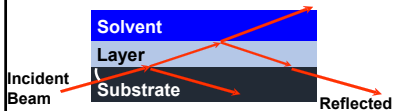
Neutron Reflectivity (NR)

Advantage of NR

Neutron beam
- distinguish isotopes (nucleus)
- high transmittance
- detect hydrogen and deuterium

- **Neutron beam from substrate**

Interface between polymer and water



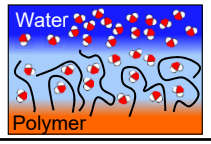
- **Distribution of absorption components**

Volume fraction of mixture from the contrast of SLDs

For example,,,

ρ(layer) = ρ(polymer)×$\phi_{polymer}$ + $\rho(D_2O)$ ×ϕ_{D2O}

Concluded….



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This Work

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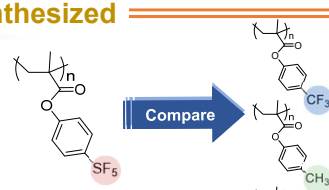
Synthesized



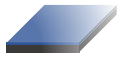
Poly(4-Pentafluorosulfanylphenyl methacrylate)(P(SF_5))

Poly(4-Trifluoromethylphenyl methacrylate)(P(CF_3))

Poly(4-Methylphenyl methacrylate) (P(CH_3))

Poly(4-Phenyl methacrylate) (P(H))

Spin-coating



Thin film

Surface properties

Fluorine-containing functional groups (-SF_5, -CF_3)

Affect?

Surface property

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Contact angle

Table The water and ethylene glycol contact angles and surface free energy values of four spin-coated films.

Sample	Water contact angle	Ethylene Glycol contact angle	Surface free energy
	deg.	deg.	mJ/m^2
P(SF_5)	102	85	15.0
P(CF_3)	96	73	22.4
P(CH_3)	92	68	24.7
P(H)	81	57	29.0

Higher fluorine content in a side chain

P(H) **P(SF_5)**

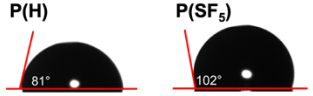

Fig. Photographs of water droplets on surfaces of spin-coated films of P(H) and P(SF_5).

Weaker affinity with water/ organic solvent

Lower Surface free energy

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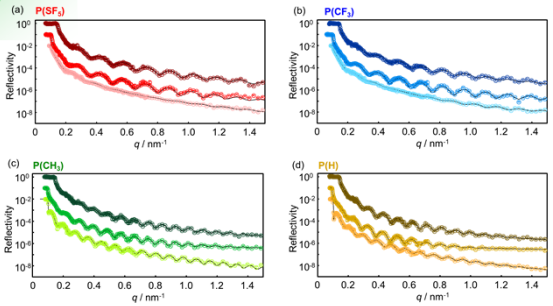
NR profiles



$P(CF_3)$, $P(SF_5)$ **Double-layer model**

D_2O or D_2O/H_2O
Polymer bulk
Adsorbed layer
SiO_2
Si

P(H), $P(CH_3)$ **Triple-layer model**

D_2O or D_2O/H_2O
Top surface layer
Polymer bulk
Adsorbed layer
SiO_2
Si

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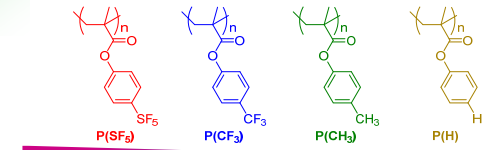
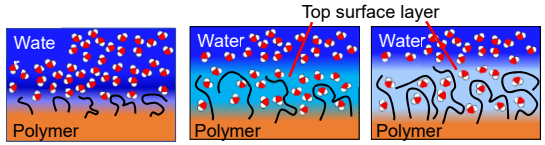
Conclusions



Hydrophobicity

Interaction with water

Water content in top surface region



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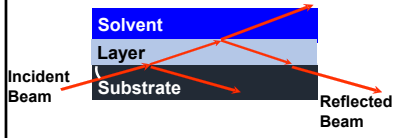

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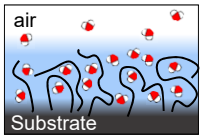

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Introduction

Vinyl polymer

Poly(substituted methylene)

C1 polymer

Mobility
Polarity

C2 polymer

Bas de Bruin, *et.al.*, *Organometallics*, **29**, 2823–2826(2010)

Side chain density

Polyacrylic acid

- Water-soluble polymer
- Paper/disposable diaper
- Paints
- Adhesive

Poly(acetic acid)

Interaction with water

Water

Side chains

Biocompatibility

Anti-icing effects

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NR @ J-PARC

Neutron reflectivity

Incident beam

Reflected beam

θ

Layer 2
Layer 1
Substrate

Identification

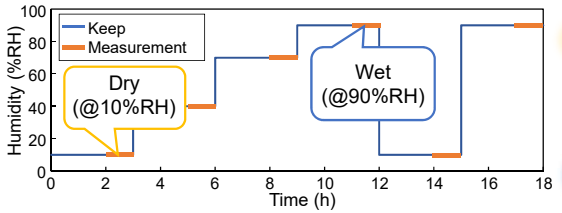
D_2O

D

H

Hygroscopicity

▸ Measurement condition (@25 ºC)



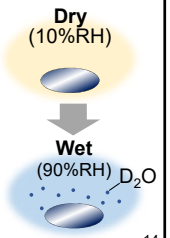


Fig. Program of humidity change at 25 ºC.

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SLD profiles

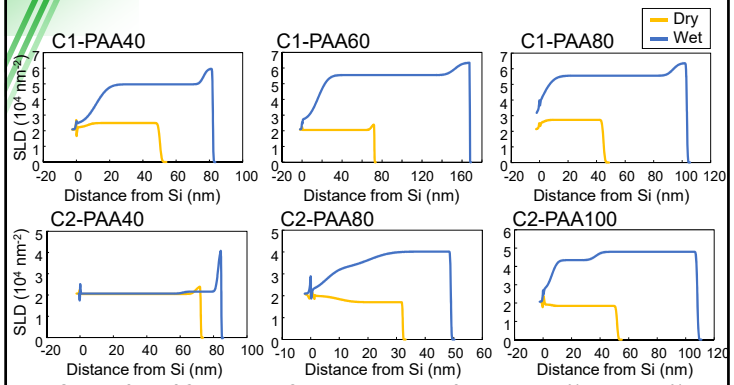

Fig. SLD profiles of C1-PAA and C2-PAA spin-coated films under 10%RH and 90%RH.

Thickness

Volume fraction of D_2O

Shape of SLD profiles

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Conclusions

Poly(substituted methylene)

High swelling

C1-PAA

Molar fraction of carboxyl side chain

C2-PAA

Different swelling properties

Water adsorption layer

Hygroscopicity

Gradation

Different swelling behavior

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Introduction

Adhesion

Epoxy resin

- ✓ Mechanical properties
- ✓ Insulation

Industrial products

Vehicle

Aircraft

・Low cost
・Light weight

After curing

Epoxy resin
Material

Thermal expansion coefficient mismatch

Residual stress

Deformation Detachment

Failure Defects

Metal → Alternative → Polymer

Residual stress measurement

Reliability

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X-ray Diffraction Stress Measurement

X-ray diffraction — $\sin^2\psi$ method

Ψ=90° Ψ=60° Ψ=30°

Parallel to the surface

Surface

Tensile stress

$\sin^2\psi$ method

Residual stress

Residual strain ε_ψ

$\sin^2\psi$

$$\varepsilon_\psi = \frac{(1+\nu_s)\sigma_r}{E_t}\sin^2\psi - \frac{\nu_s}{E_t}\sigma_r$$

ν_s: Poisson's ratio of adherend
E_t: Elastic modulus of adherend
σ_r: Residual stress
ε : Residual strain

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2θ Profiles of Laminated it.PP

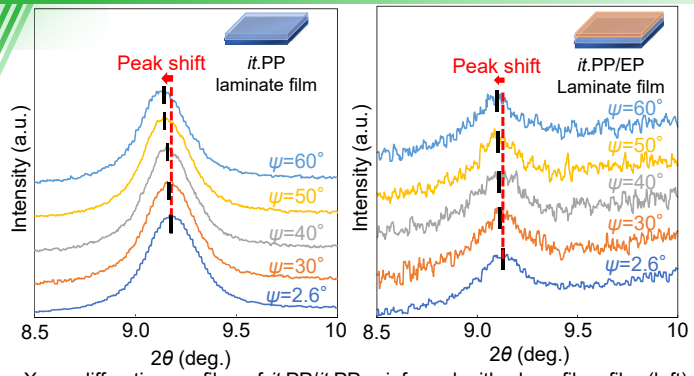

Fig. X-ray diffraction profiles of *it*.PP/*it*.PP reinforced with glass fiber film (left) and *it*.PP/EP film (right) at different azimuth angles at α=2.0° .

Tensile stress

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Residual Stress

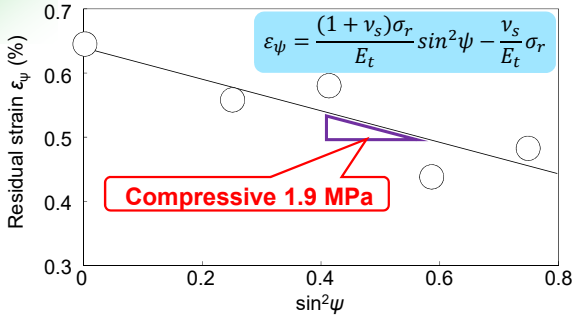
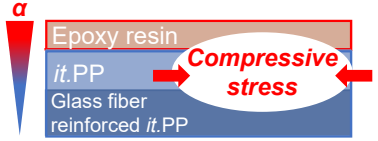


Fig. Relationship between the residual strain of the *it*.PP/EP film and $\sin^2\psi$.



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Thickness Dependence of Residual Stress

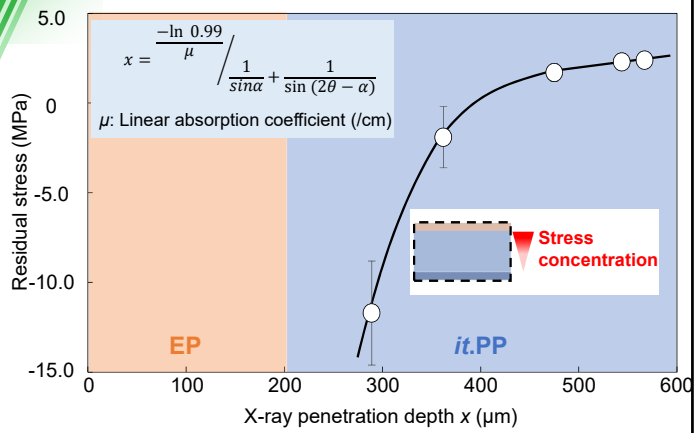

Fig. Relationship between residual stresses of *it*.PP/EP sheets with 240 s plasma treatment and X-ray penetration depth.

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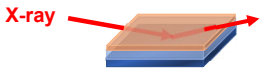
Conclusions

➢ *X-ray diffraction stress measurement*

- Reflection method



Compressive

Polymer-polymer interface

- Dependence of *it*.PP thickness

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Summary

Measurements with Synchrotron Radiation

What? How?

Observation of undetectable structure and interaction

1. 水をはじく高分子とはじかない高分子の界面
2. 水を吸う高分子の内部構造
3. 高分子の接着界面に発生する応力

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Acknowledgements

西野 孝 教授

謝 イチクン
冨岡 美里
細見 亮介

KEK 山田 悟史 准教授
瀬戸 秀紀 教授
防衛大 根本 文也 助教

Aquatic Functional Materials

CREA

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