Clay Film Technologies

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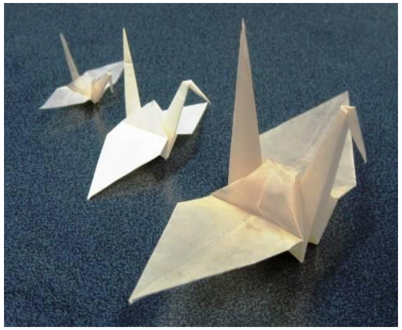
(AIST)



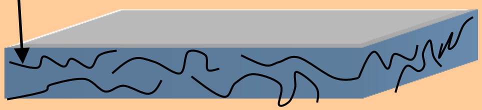
Agenda

- Concept
- Properties
- Applications
- Acknowledgement

Concept

Concept of the clay-based-film

Filler (clay) ～8%



Gas barrier performance improved from twice to five times.

Clay-plastic nanocomposite

Heat durability and gas barrier performance are expected to improve if the material is mainly made of clay.

Lateral dimension up to a few hundred nm

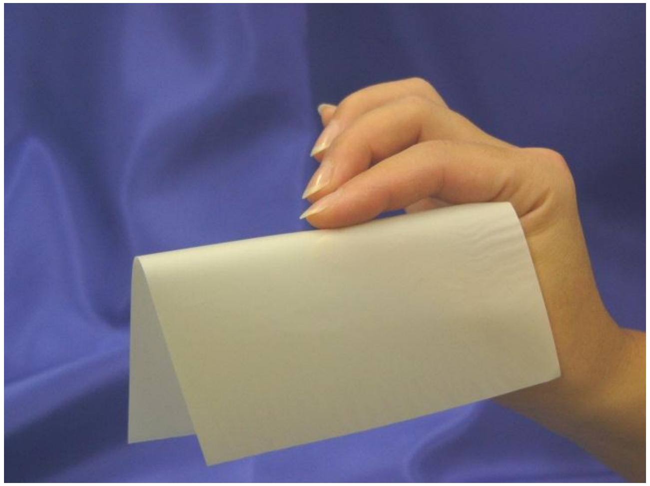
40,000 stacking=40μm thick
50,000,000 array=50m long

Thickness c.a. 1nm

Ideal structure of the self-supported film

Bentonite paper: E.A. Hauser and D.S. Le Beau, J. Phys. Chem. 42, 961 (1938).

Outlook

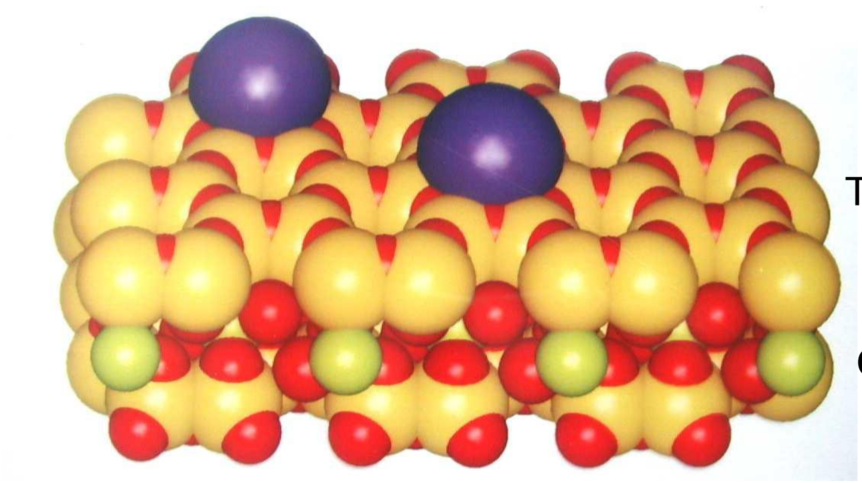


Non-transparent type
: Made from natural clay

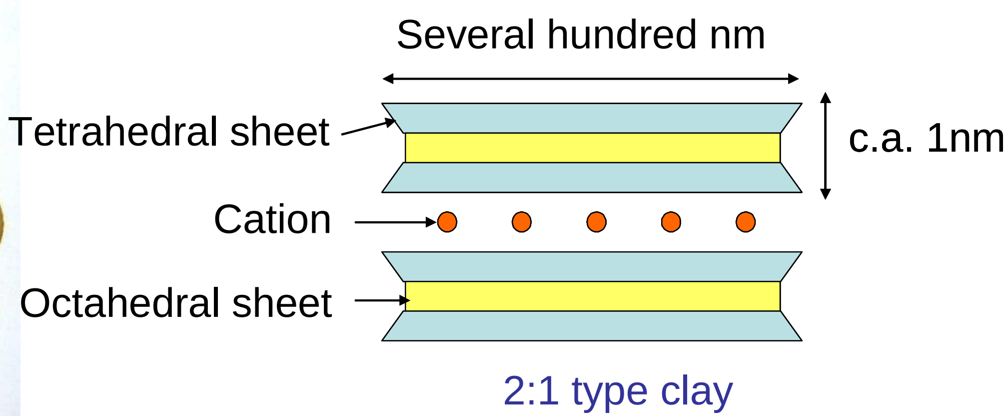
Transparent type
: Made from synthetic clay

Claist®

Layer structure of clay →2:1 type phyllosilicate



Surface structure of Cs-smectite



: $Na_{0.33}[(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2]$

montmorillonite

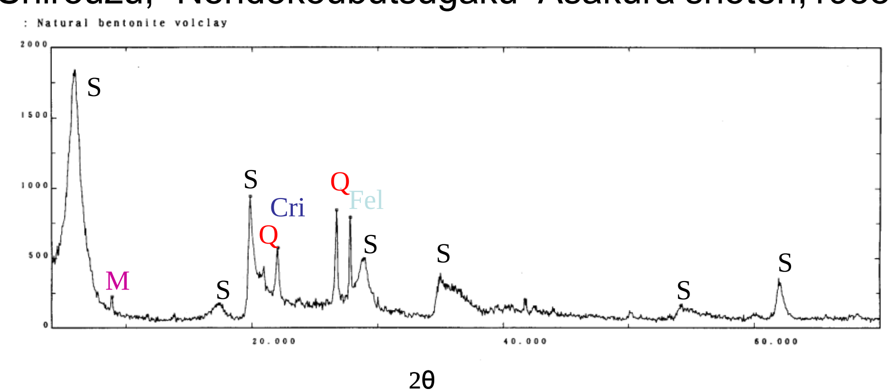
Natural clays which form films

Bentonite mine in Miyagi, Japan

Various clays and its layer charge

Mineral	Layer charge	CEC(meq/100g)
mica	1	10～15
Sericite	0.85	
Illite	0.75	
Vermiculite	0.66	100～150
Smectite	0.33	60～100
Talc	0	

H. Shirouzu, “Nendokoubutsugaku” Asakura shoten,1988



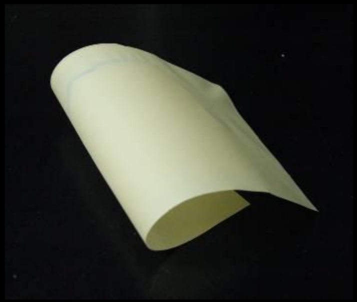
XRD chart of a natural bentonite (Volclay)

S:smectite、M:mica、Q:quartz、Cri:cristballite、Fel:feldsper

Film formability comparison between natural and synthetic clay

Natural

Montmorillonite (Kunipia P)



Montmorillonite (Tsukinuno)

Hectorite (SHCa-1)

Synthetic

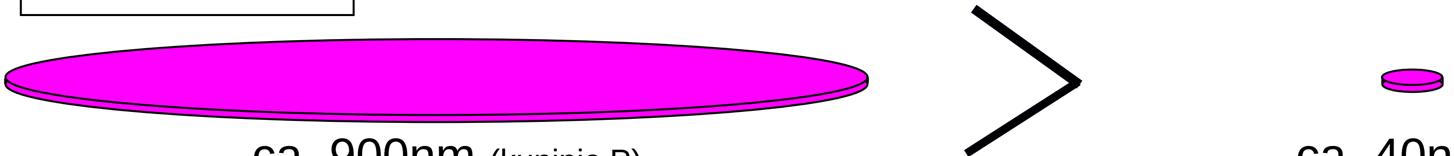
Hectorite (Laponite)

Saponite (Smecton SA)

Stevensite (Smecton ST)

Hectorite (Thixopy)

Particle size



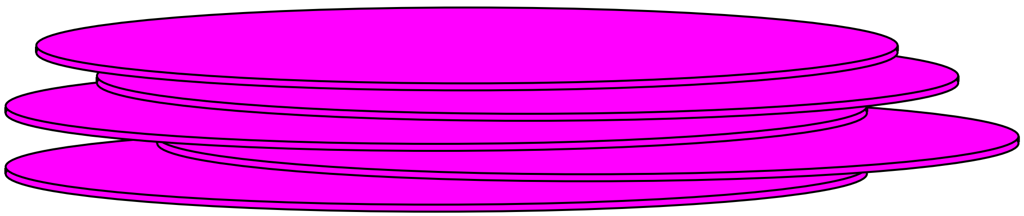
ca. 900nm (kunipia P) > ca. 40nm (Smecton ST)

Effect of enlargement of clay particles

1) <u>Enhance film formability</u>

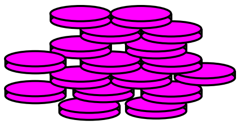
In general, natural clay show higher film formability than synthetic clay.

Natural clay



Average aspect ratio (a/b) =320

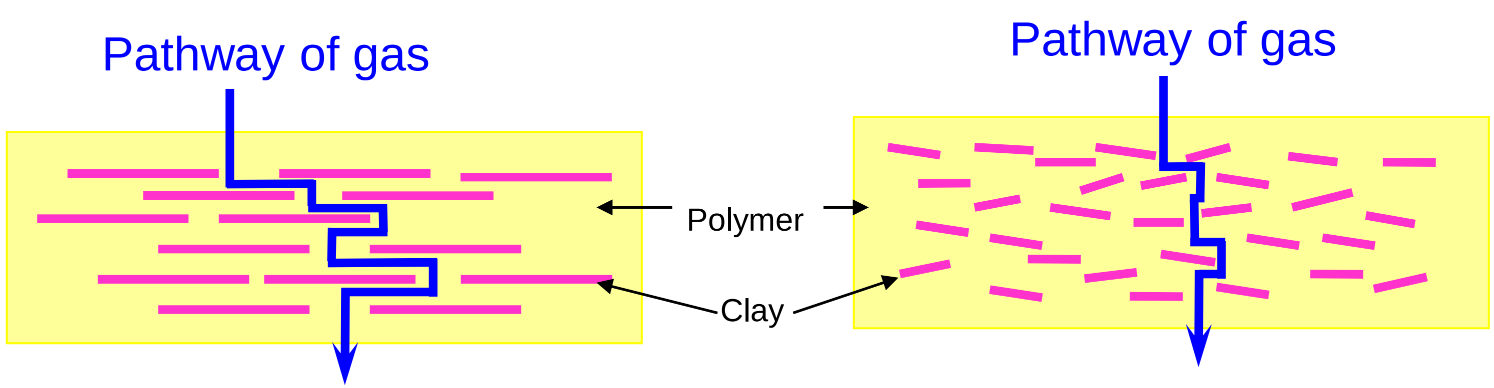
Synthetic clay



Average aspect ratio (a/b) =50

2) <u>Enhance gas barrier property</u>

The composite with large particle is expected to be with high gas barrier property.

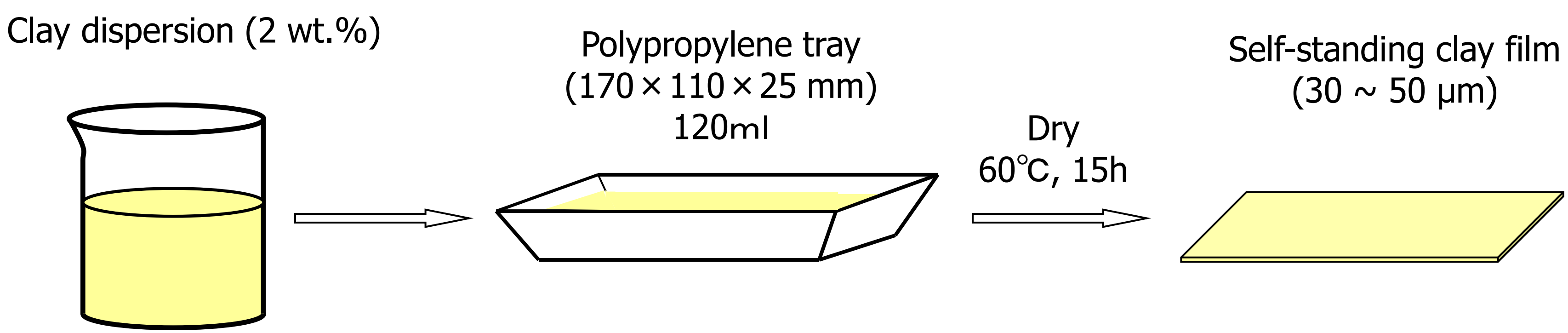


Experimental

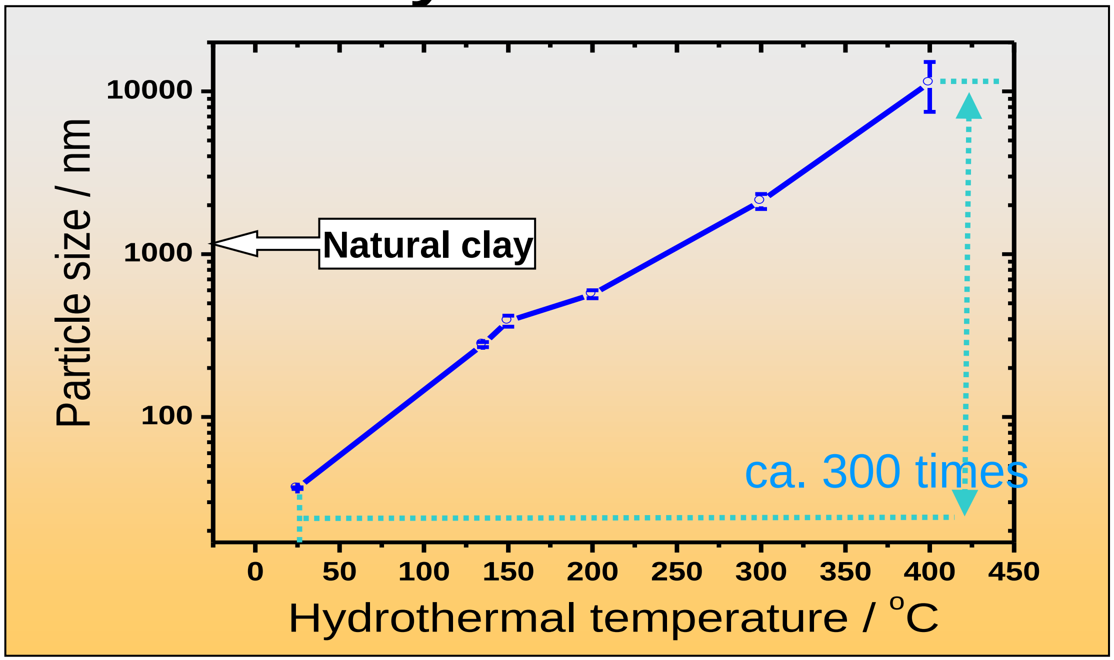
- **Clay used**: Synthetic stevensite
  (Smecton ST, Kunimine Industries, $Na_{0.33}[Mg_{2.83}]Si_4O_{10}[OH]_2$)

- **Hydrothermal treatment**: Batch-type autoclave (500mL), Suspension of clay (250mL, 0.2wt.%), 135～400℃, 10h (temperature programming rate: target temperature/4h)

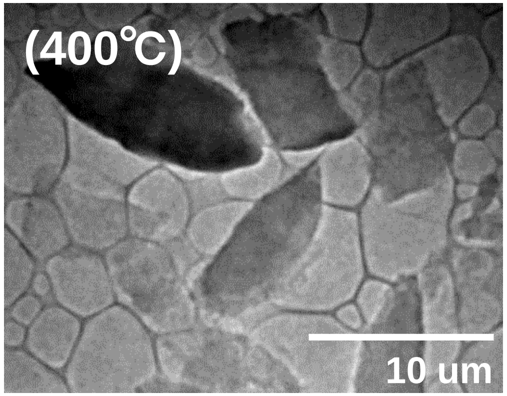
- **Film formability test**

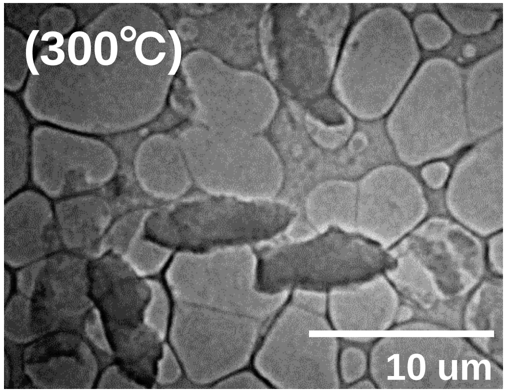


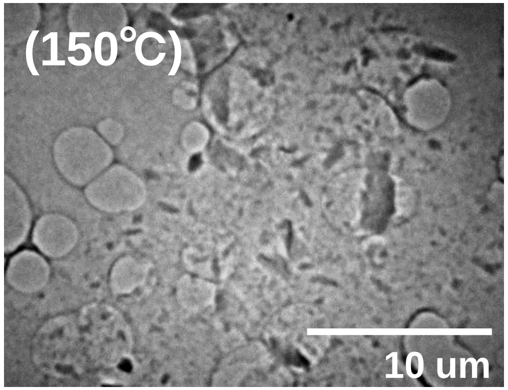
Particle enlargement of clay by a hydrothermal treatment

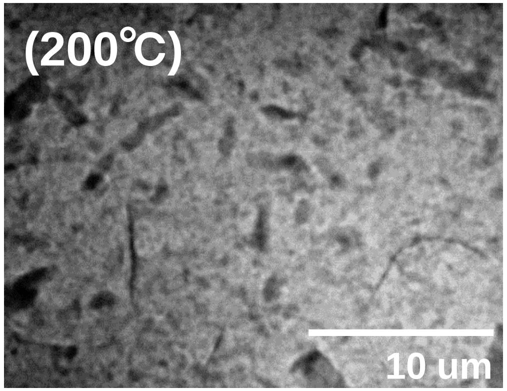


Hydrothermal treatment is an effective technique for particle enlargement !





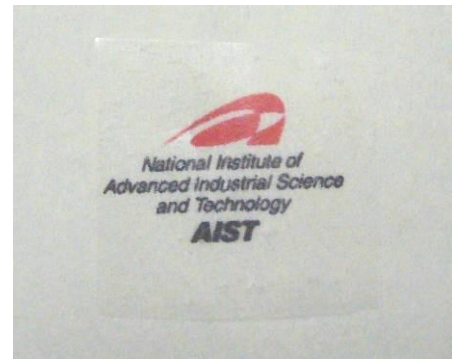


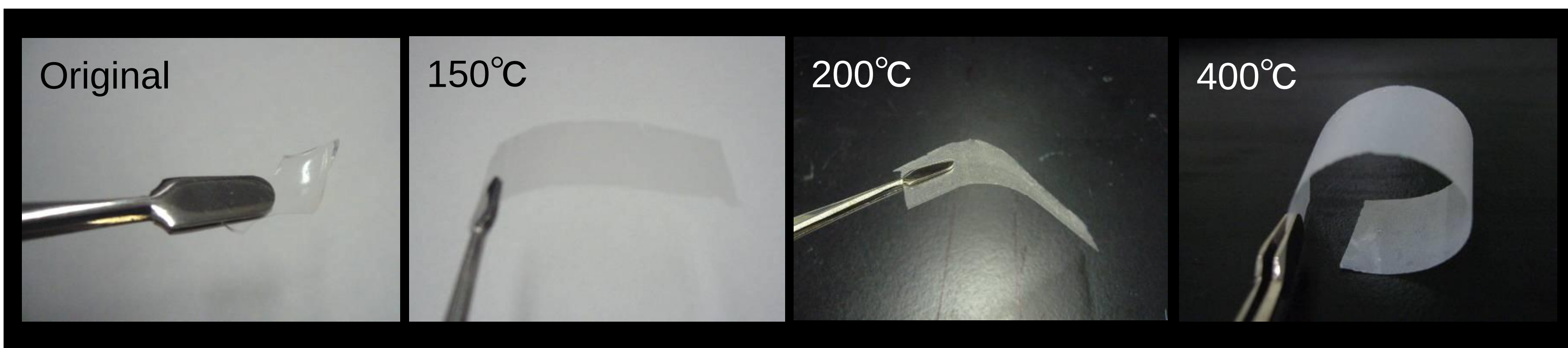


Improvement of film formability by hydrothermal treatment

Original

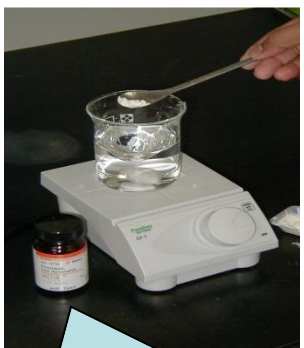
Hydrothermally treated





Typical preparation procedure of clay-based-film

mixing → **spreading** → **drying** → **peeling**



curing

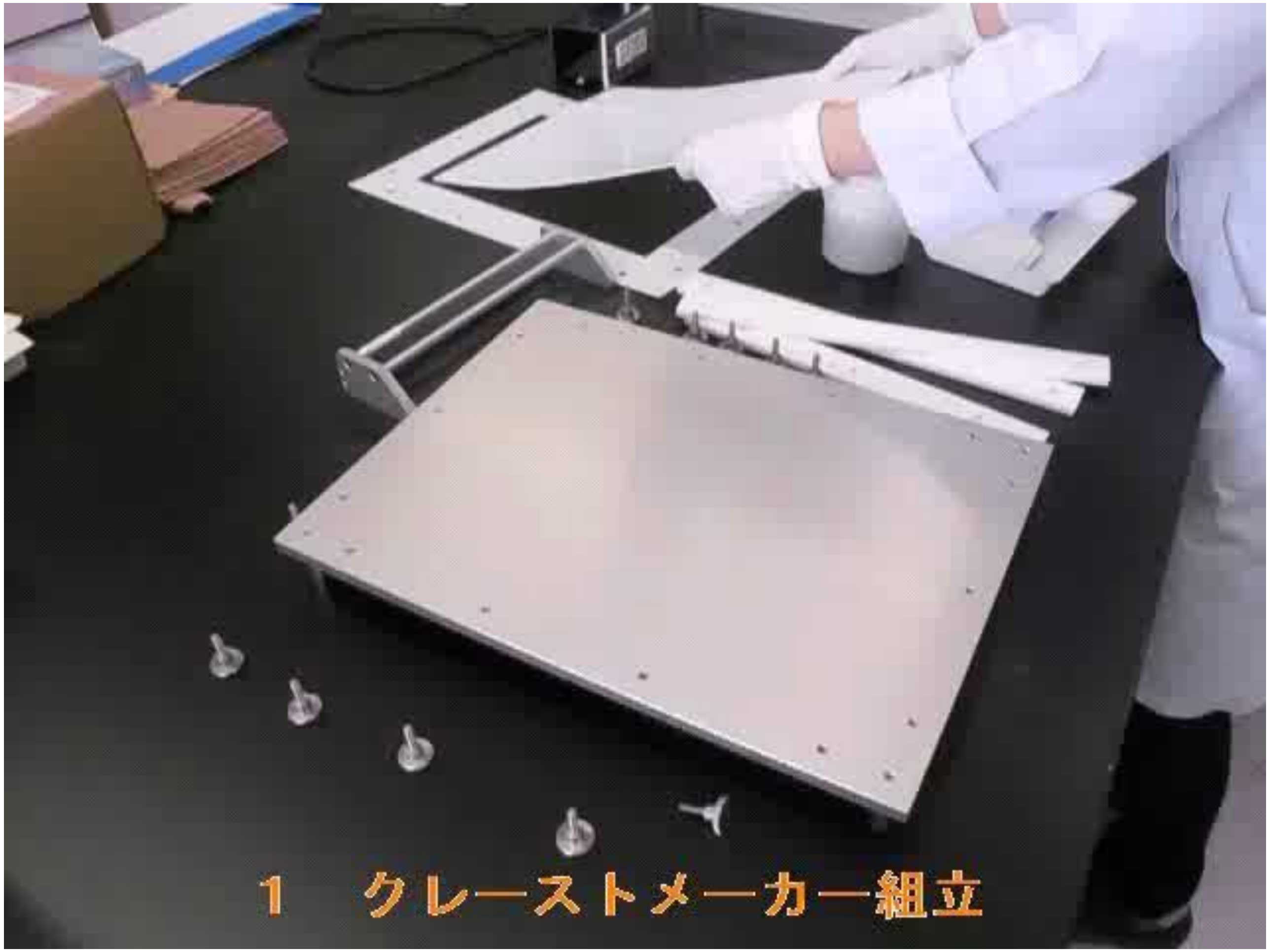
further processing

Surface treatment
Lamination
etc.

Clay: natural, synthetic, organoclay
Additive: plastics, fibers, particles

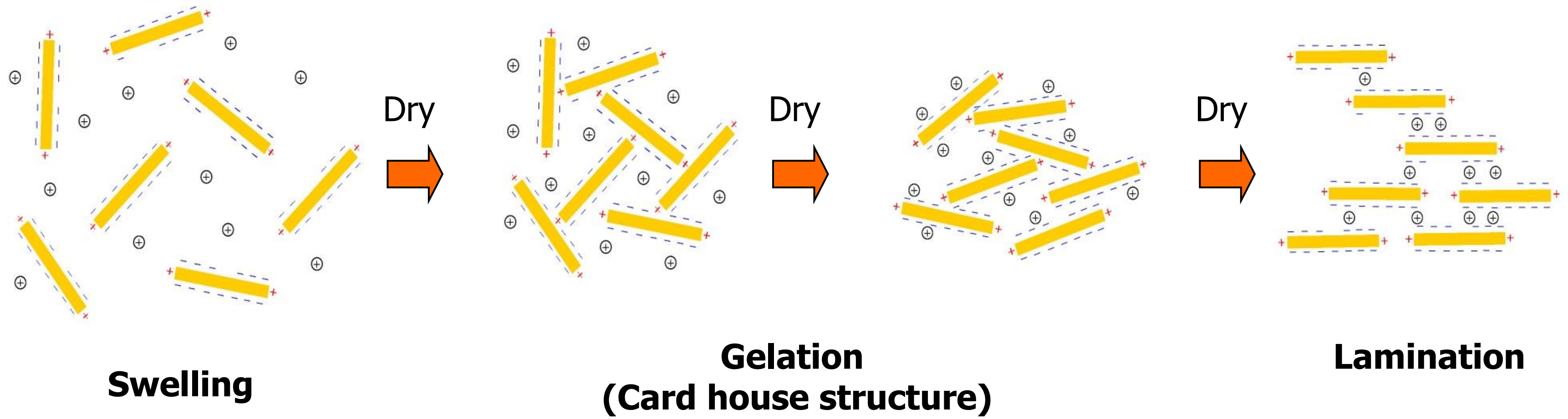
Liquid :water(1st generation)
toluene(2nd generation)
mixed solvent (3rd generation)

Clay film preparation

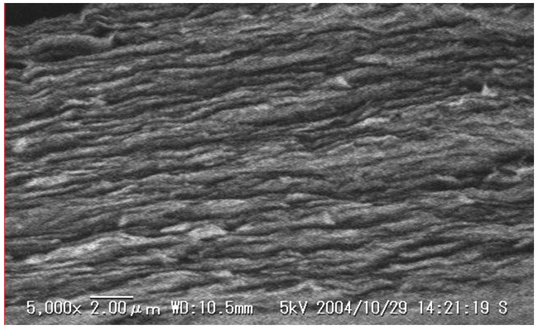


Mechanism of the film formation

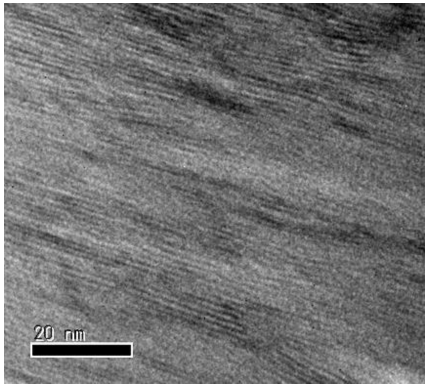
Steps of the film formation



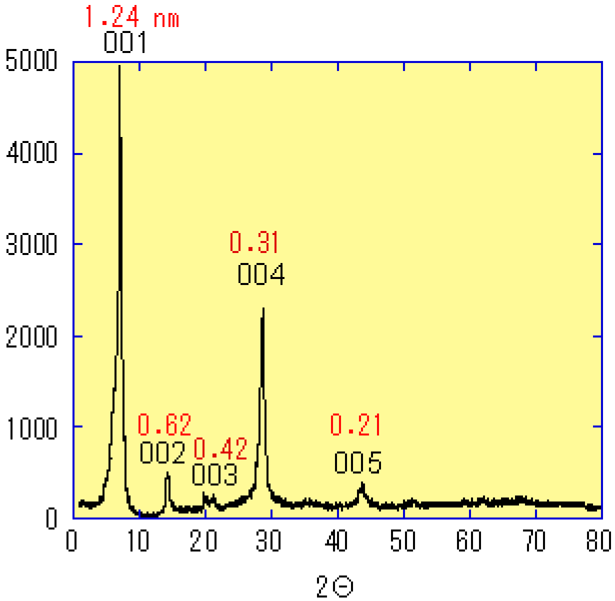
Lamella structure of clay films



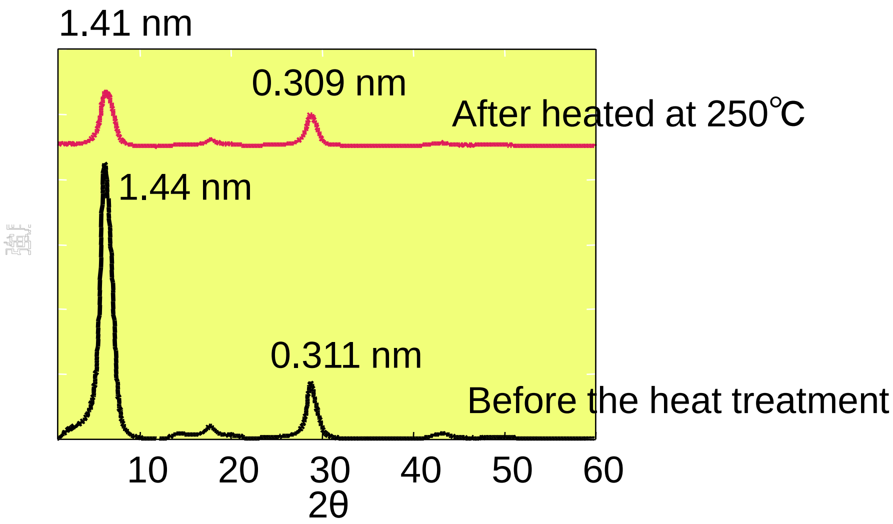
SEM section view



TEM section view



XRD pattern of clay film without organic additive



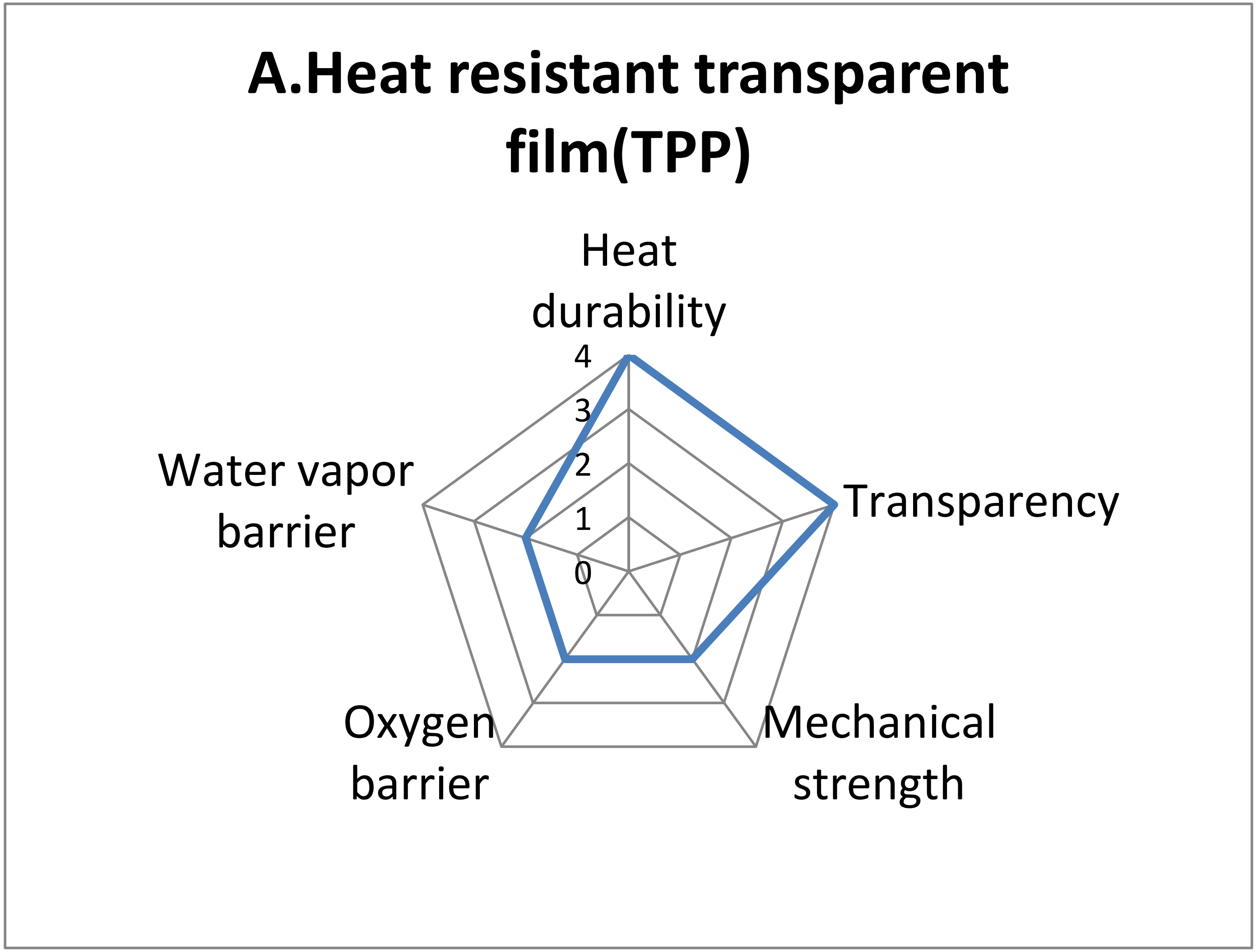
XRD patterns of clay film type ST with approximately 10 wt% ε-caprolactam

Properties

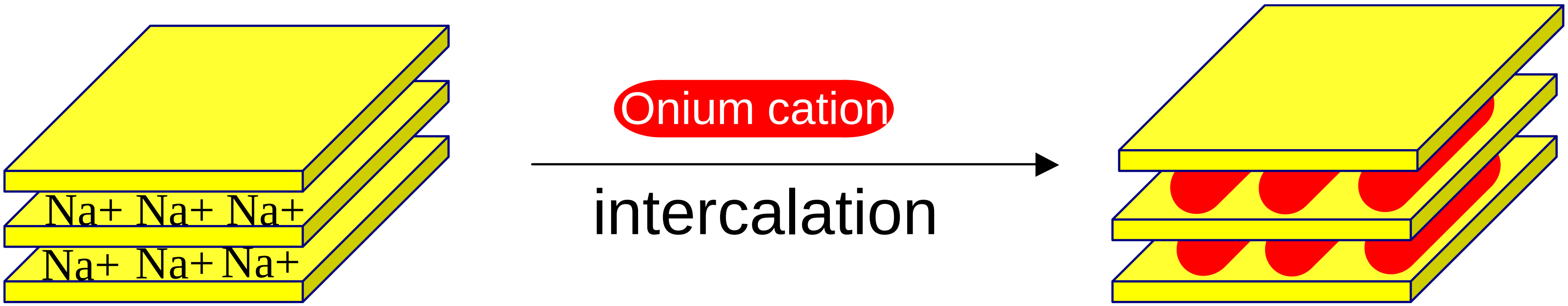
Properties

Various films

- A. Heat resistant transparent film(TPP)
- B. Water vapor barrier film(SN)
- C. Heat resistant insulation film
- D. Food packaging(Oxygen barrier)
- E. Water vapor barrier coating

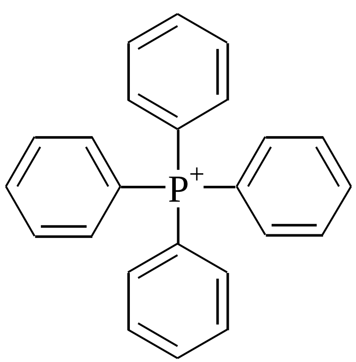

A.Heat resistant transparent film(TPP)
Heat durability
4
3
2
1
0
Transparency
Mechanical strength
Oxygen barrier
Water vapor barrier

Heat resistant transparent film (TPP)



Clay (Hydrophilic)

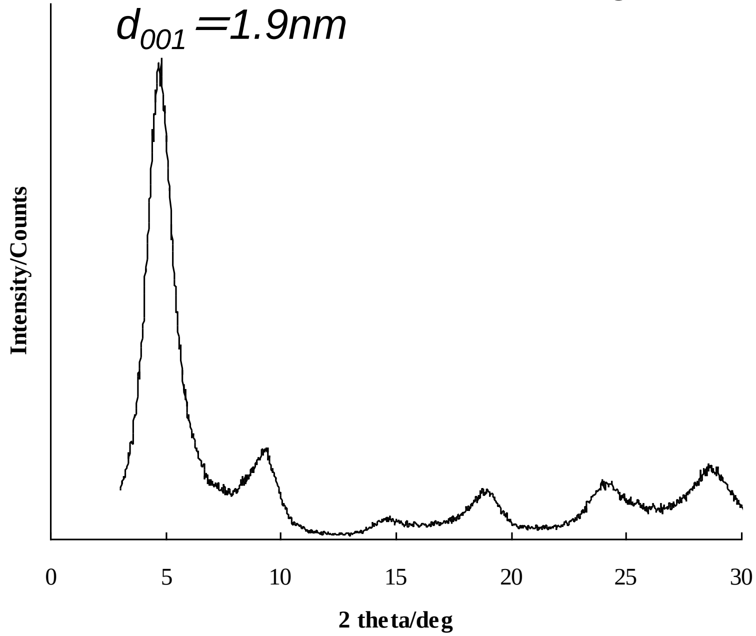
Organoclay (Hydrophobic)



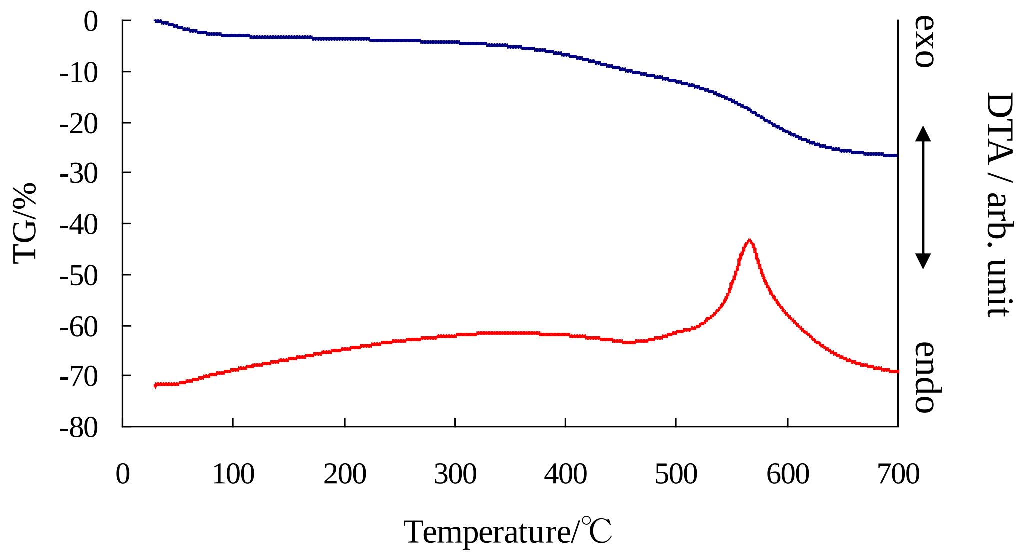
Tetraphenyl phosphonium cation (TPP)

K. Kawasaki, T. Ebina et al, *Appl. Clay. Sci.,* 2010, **48**, 111-116.

Flexible TPP-SA film
（Total light transmittance 90%、HAZE value 50%）

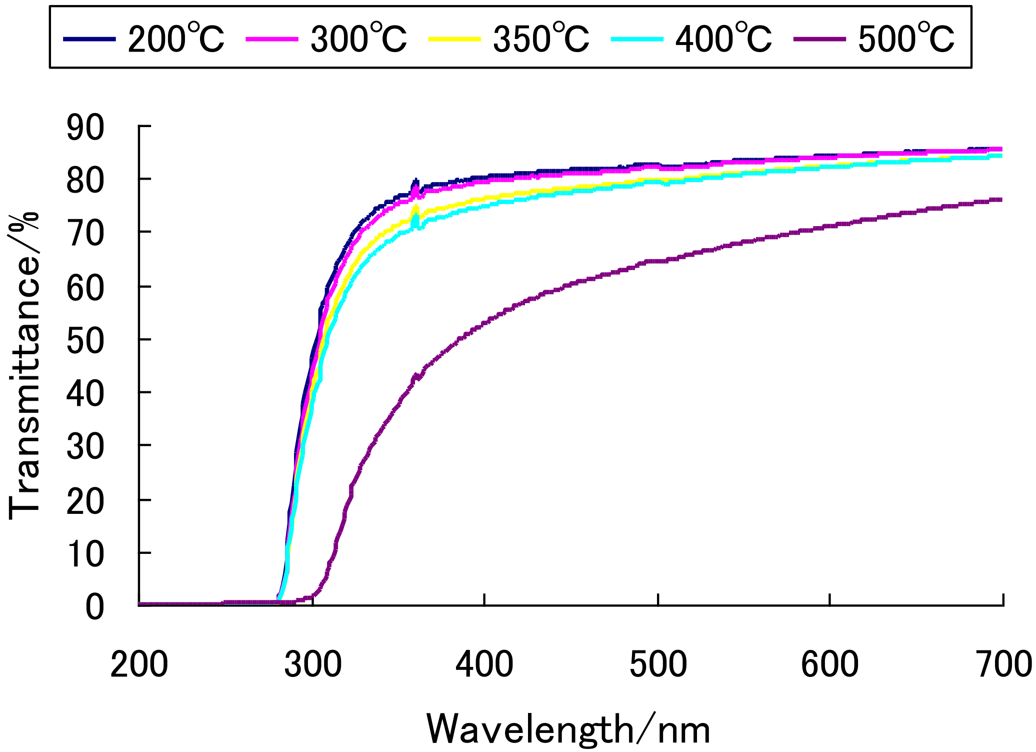


XRD spectra of TPP-SA film



TG-DTA curve of TPP-SA film

Tomoegawa Co.



UV-visible light transmittance of TPP-SA films treated at different temperature
(Heating rate of 5℃/min.)

200℃

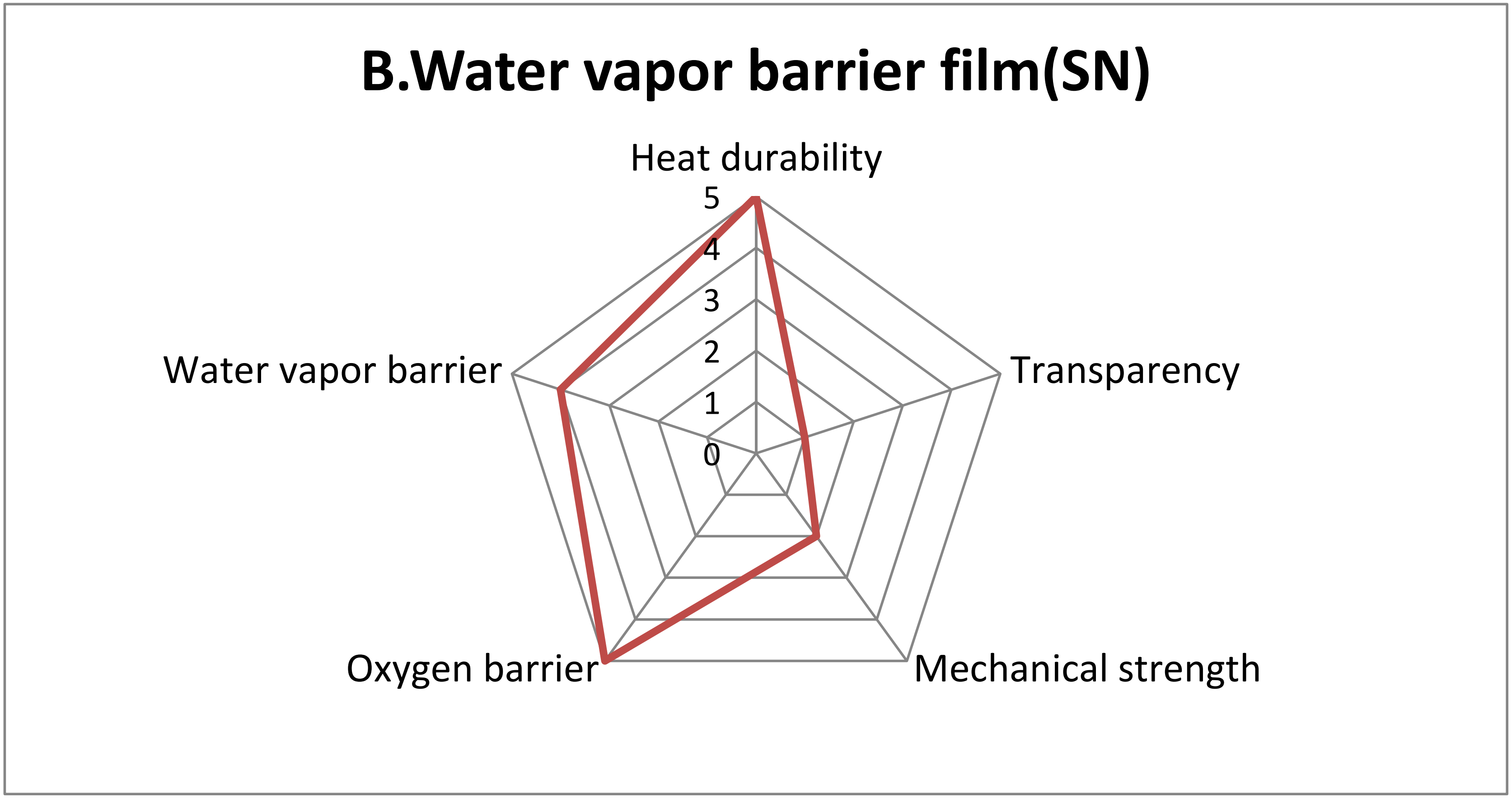
300℃

350℃

400℃

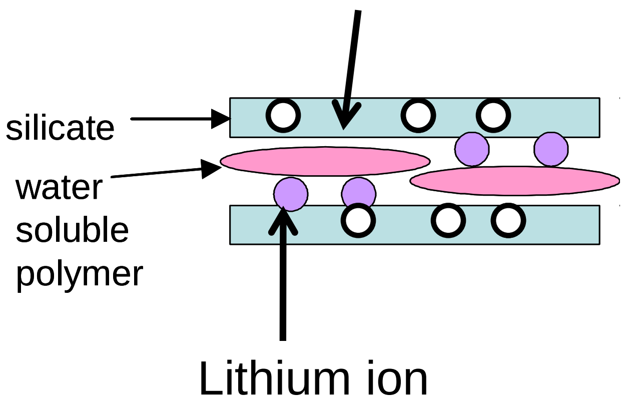
500℃

・TPP-SA films heated up to 350℃ or 400℃ exhibited some coloring.
(Their light transmittances of visible light (500nm) were 80% and 79%)

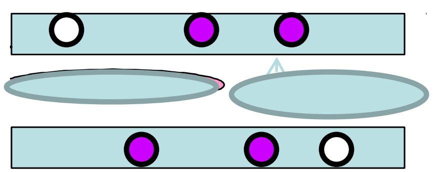

B.Water vapor barrier film(SN)
Heat durability
Transparency
Mechanical strength
Oxygen barrier
Water vapor barrier
5
4
3
2
1
0

Water vapor barrier film (SN)

Clay with vacant and positive charge in the octahedral site (Montmorillonite, and Stevensite)

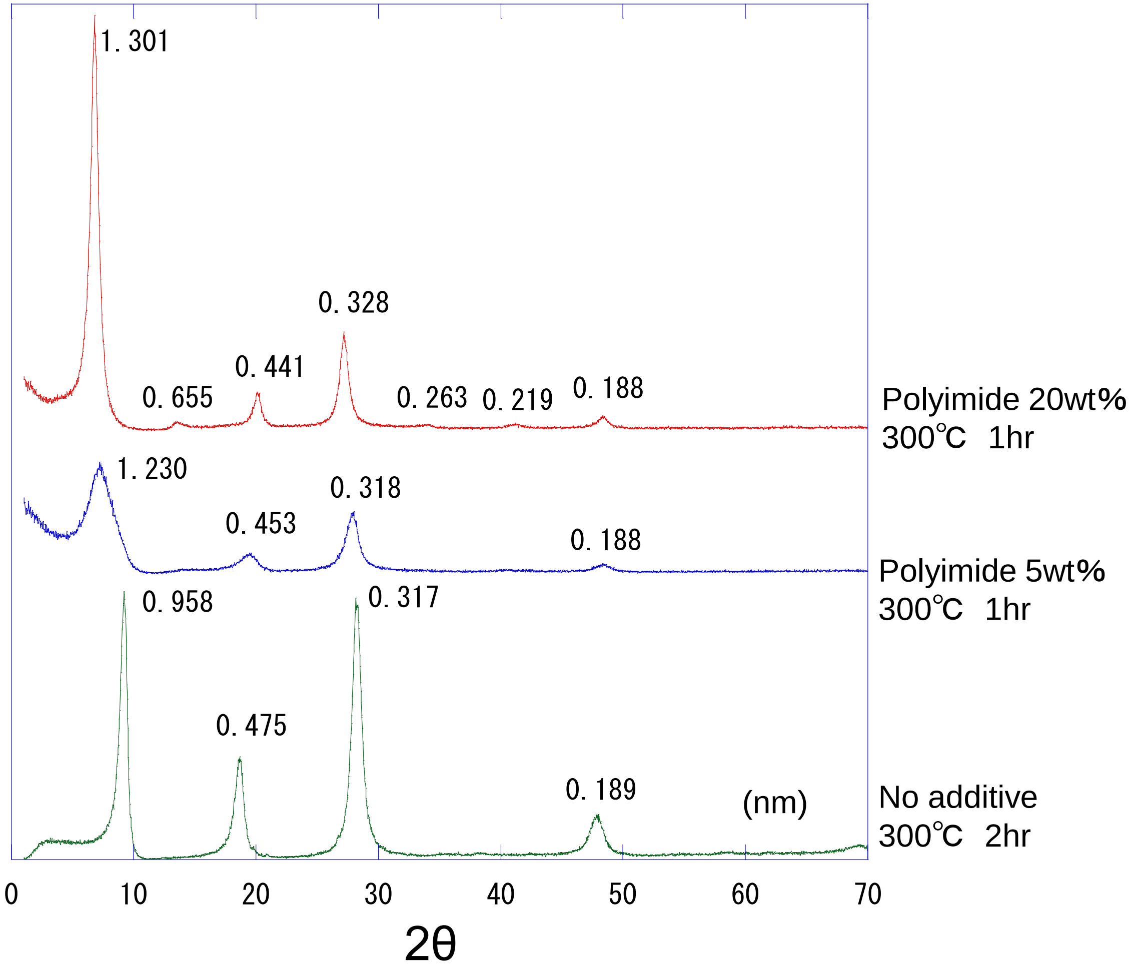


Heating
>230℃



①Migrate lithium into the crystal structure
②Binder changes to be waterproof

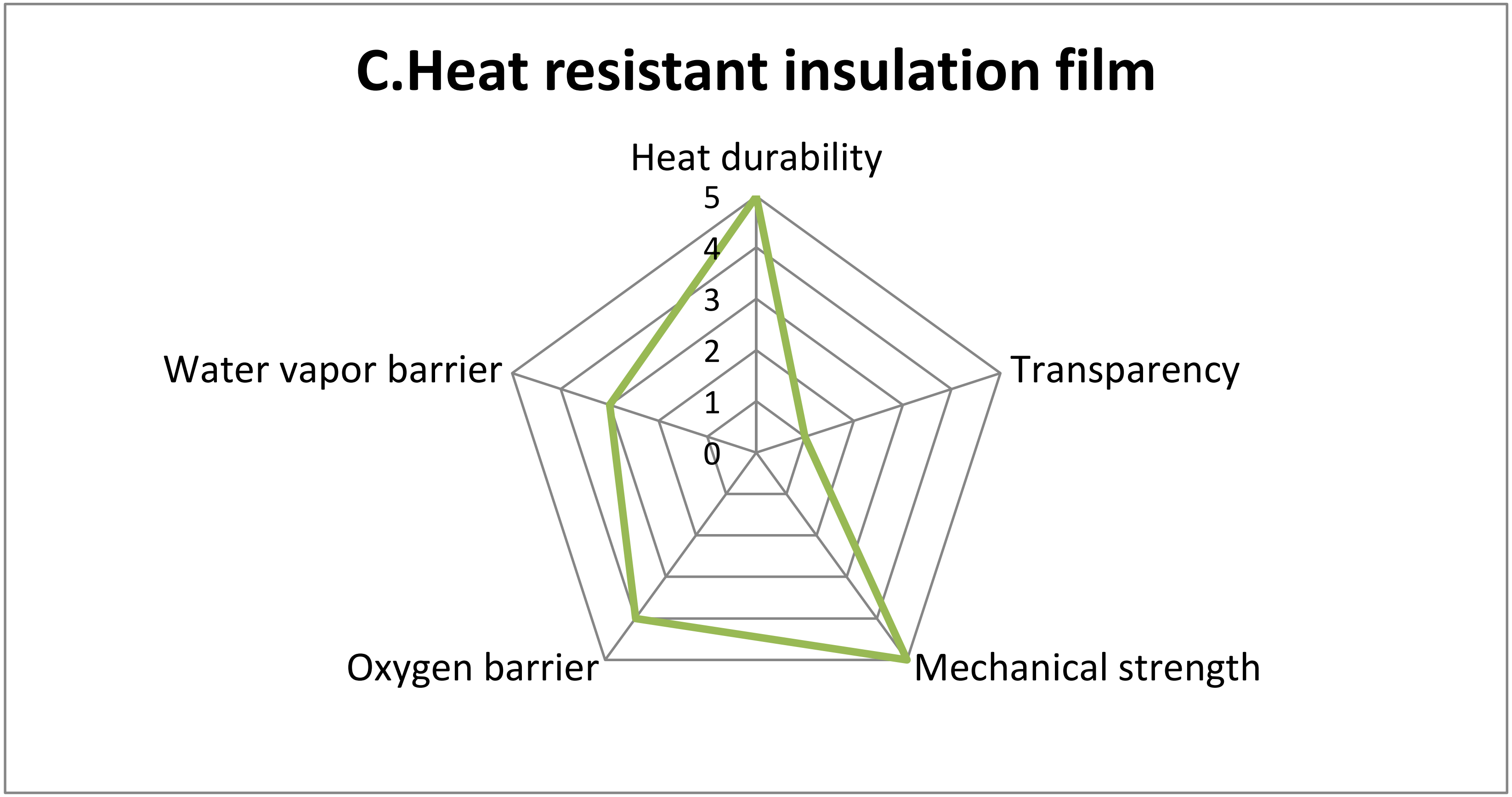
XRD chart of SN film



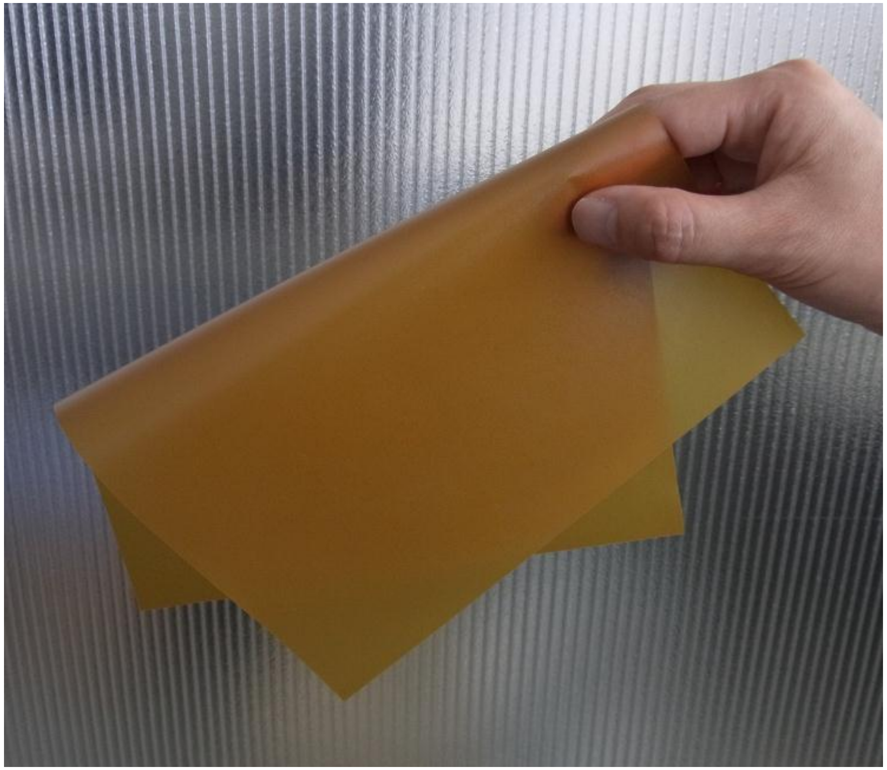
Properties of SN film

Mandrel bending test	＜2mm		Thickness15μ m
Water adsorption	0.20%		40℃90%RH
Chemical resistance	Acetone	3.98%	25℃
	IPA	10.63%	25℃
	Ethylene glycol	12.20%	25℃
Gas barrier property	Oxygen	＜0.1 cc/m^2・day・atm	25℃
	Water vapor	0.0012 g/m^2・day[1)] 0.027 g/m^2 day[2)] 0.0046 g/m^2 day[3)] ＜0.01 g/m^2 day[4)]	85℃ 85%RH 40℃ 90%RH 40℃ 90%RH 40℃ 90%RH

1) API-MS method, 2)Mocon Aquatran、3)Technolox Deltaperm 4)GTRtec Gas chromatograph method

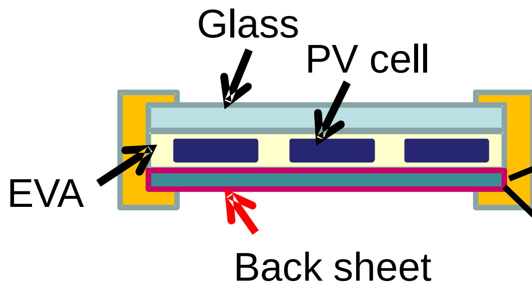

C.Heat resistant insulation film
Heat durability
5
4
3
2
1
0
Transparency
Mechanical strength
Oxygen barrier
Water vapor barrier

Newly developed heat-resistant film (Toughclaist)

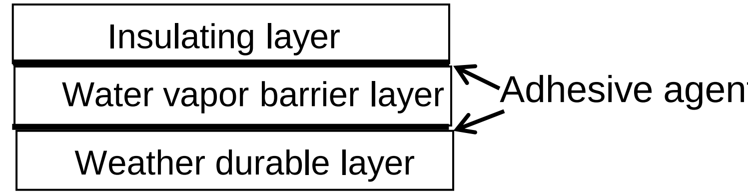


Outlook of Toughclaist

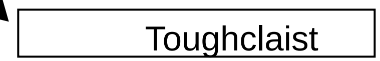
A 57cm width TP film



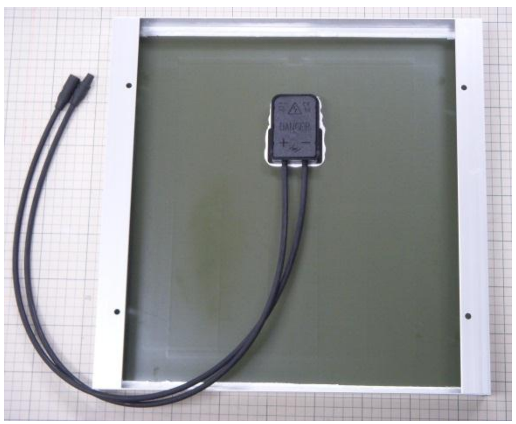
Crystal Si solar cell



Structure of typical back sheet



Proposed back sheet structure

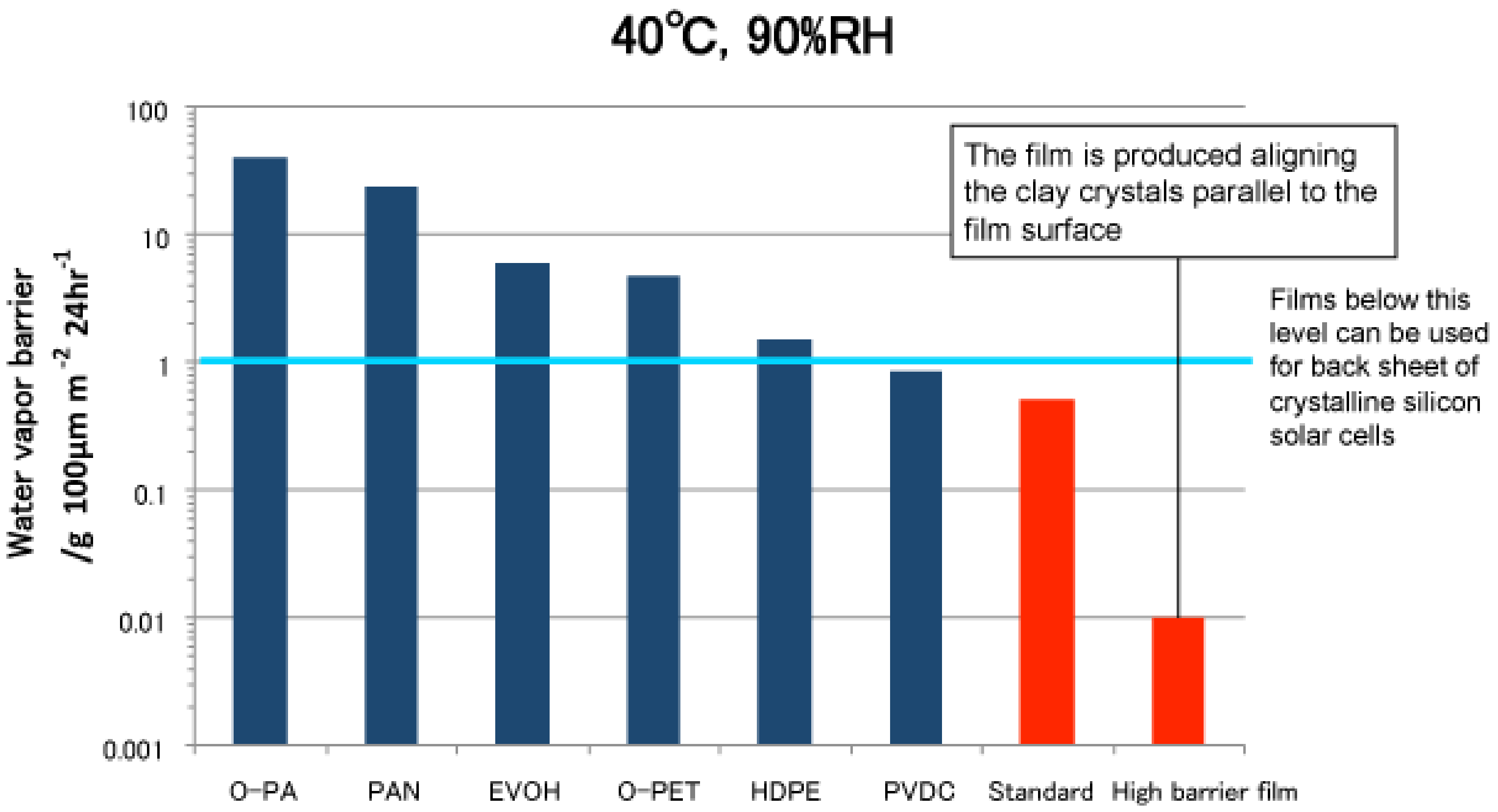


PV module (rear)

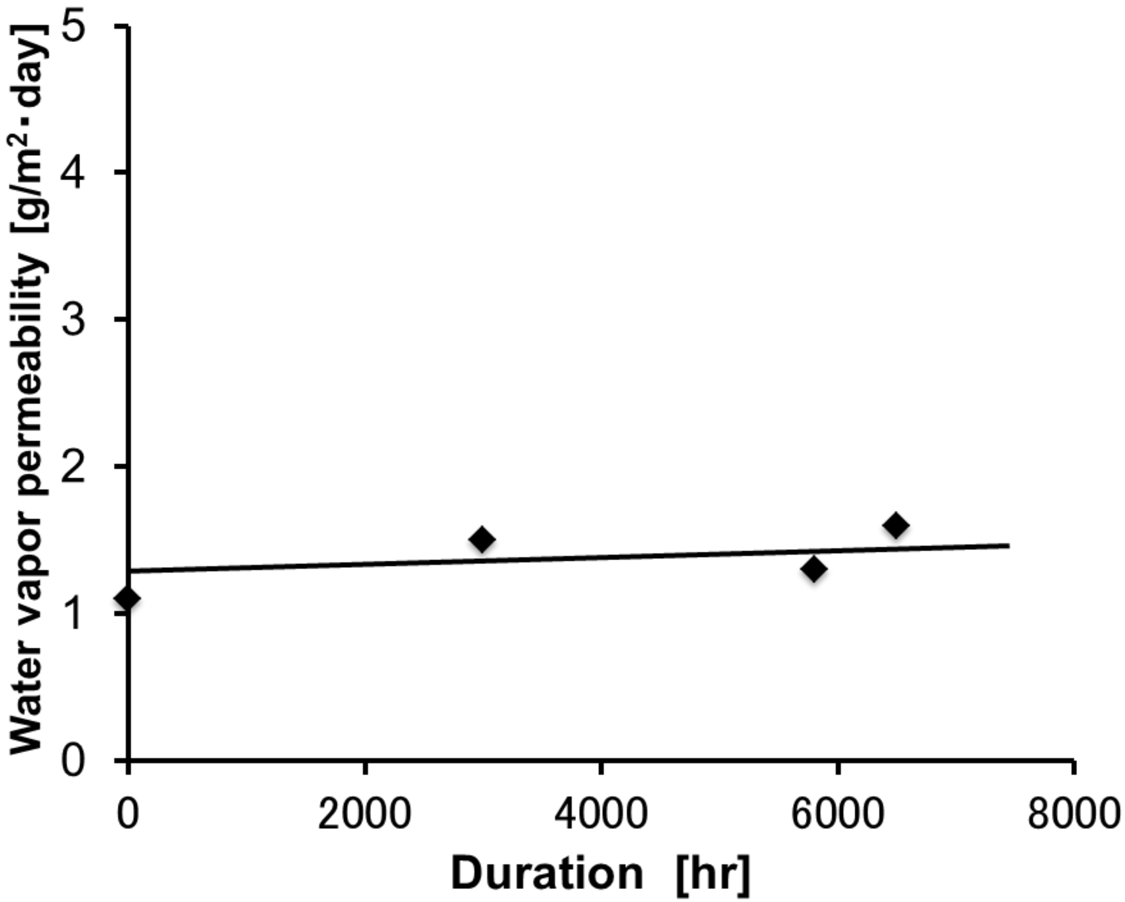
(front)

Proposed structure of a solar call using Toughclaist as a backsheet

Comparison of water vapor barrier properties of typical films



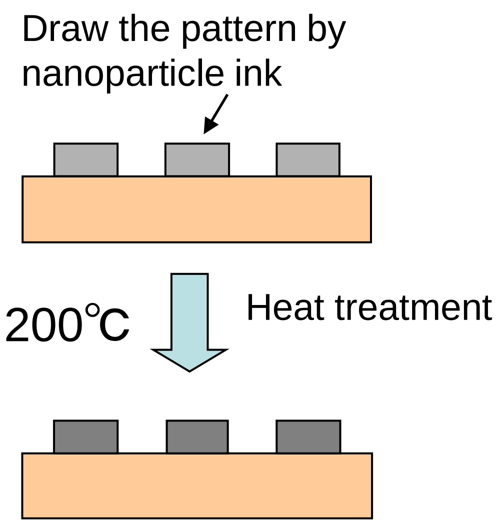
Source: Clayteam technical book (partially revised)

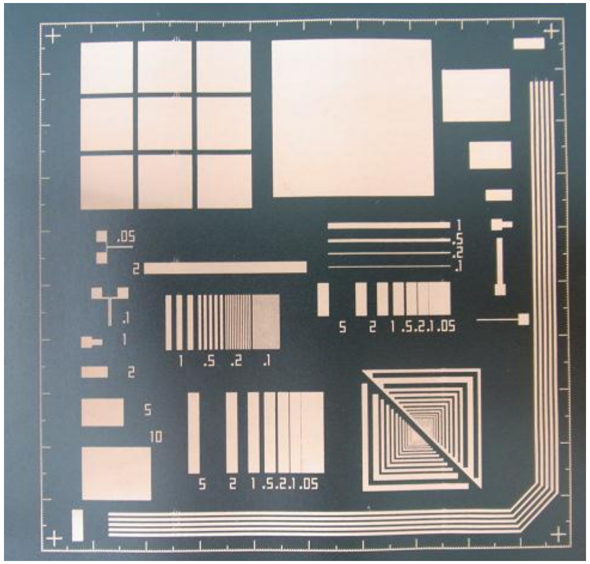


Time course change in water vapor permeability of Toughclaist
(Dump heat condition 85℃, 85%RH,
WVP measurement at 40℃, 90%RH)

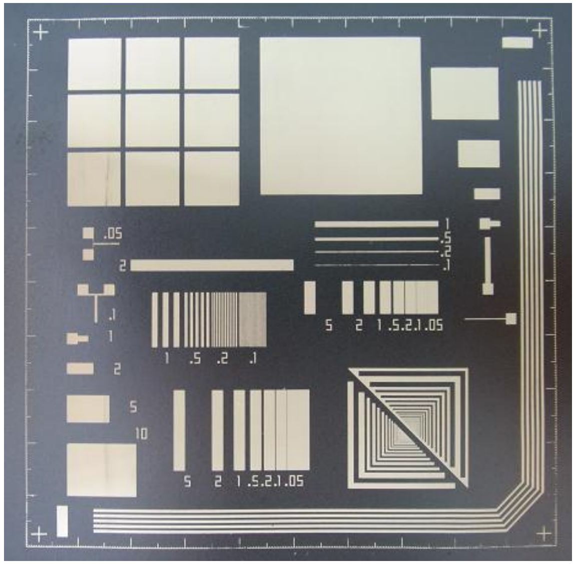
Example of electronic circuits drawn by a printing method on Toughclaist (film size 8 cm×5 cm)

Screen printing

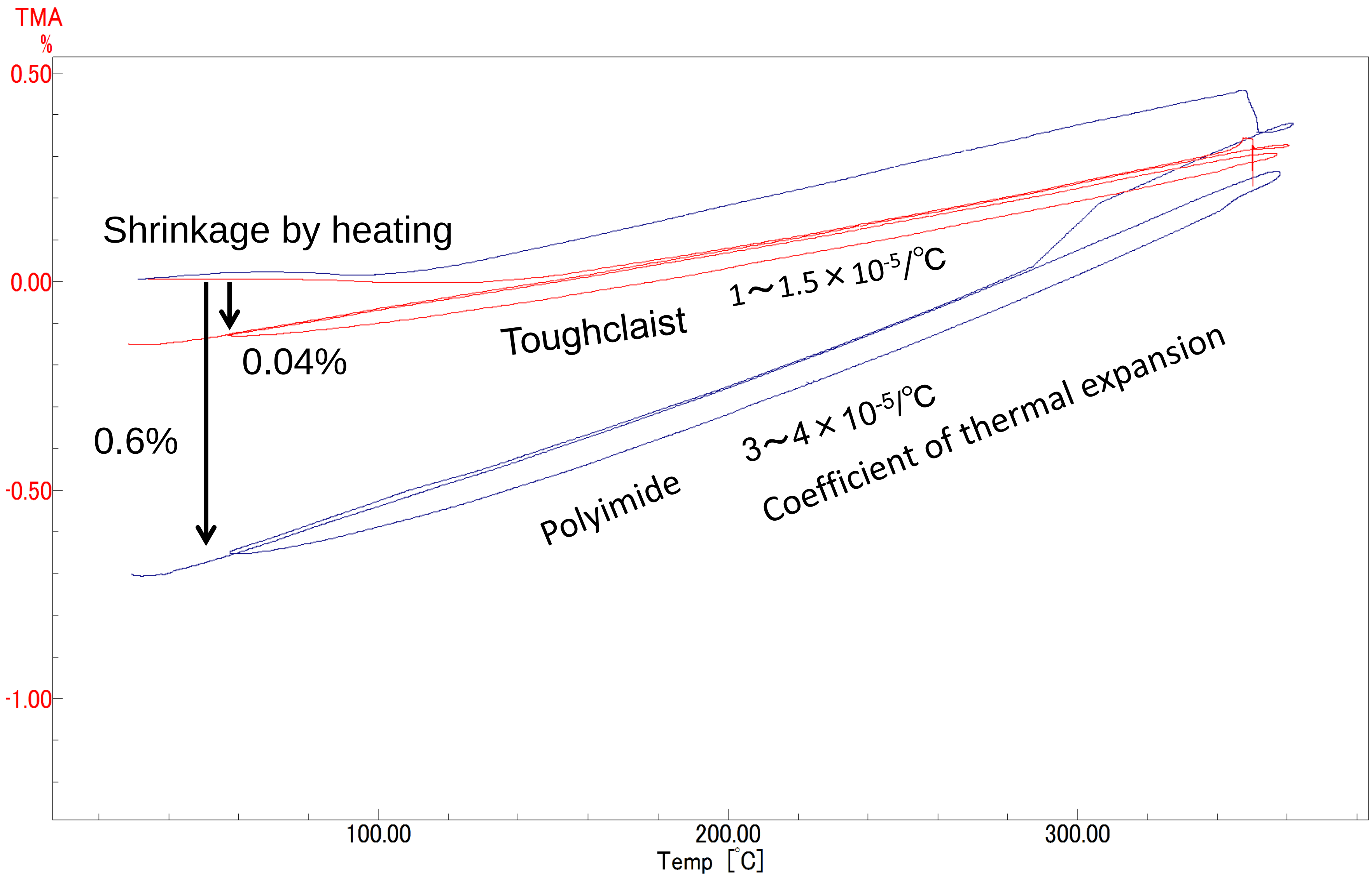




Cu ink used

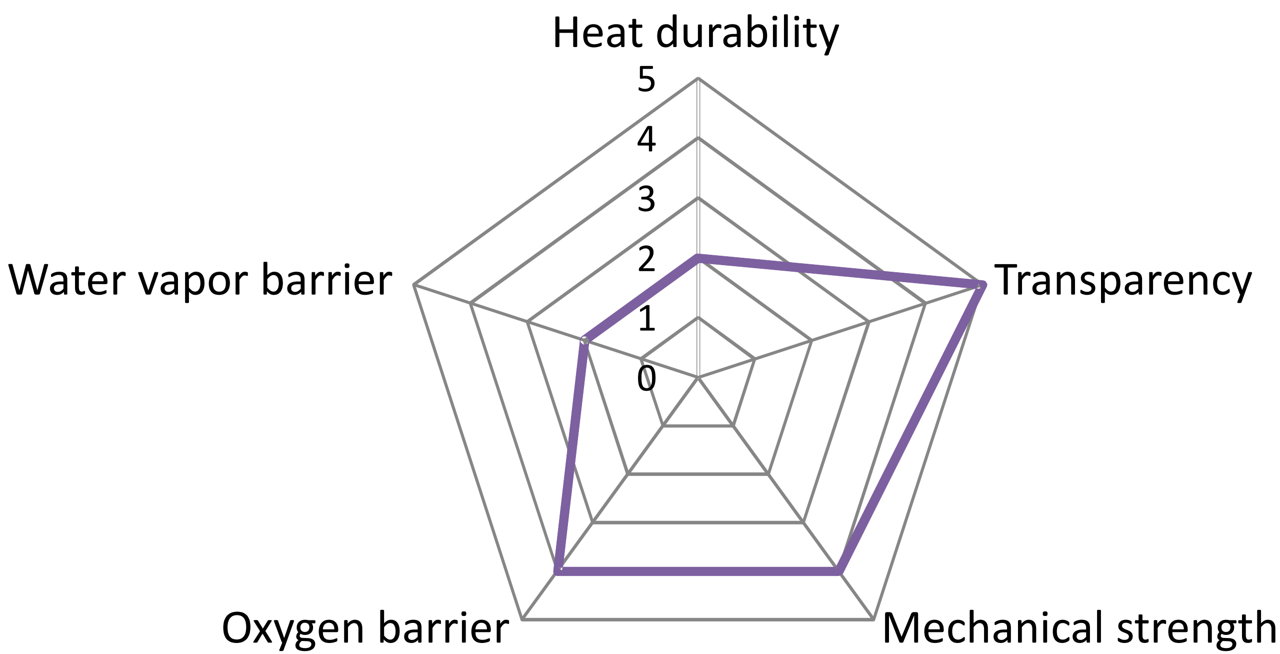


Ag ink used

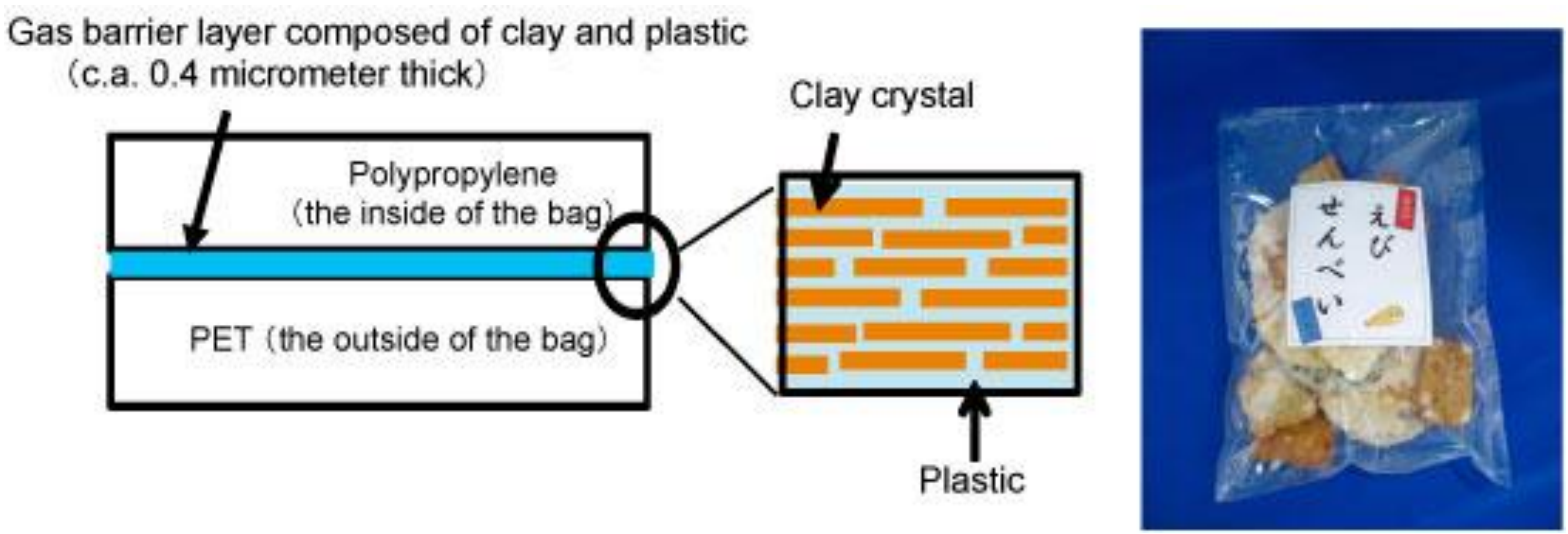


Comparison of TMA curves between polyimide film and Toughclaist

D.Food packaging(Oxygen barrier)



Food packaging film



A cross section of the developed oxygen gas barrier film (left), an enlarged view of the gas barrier layer (middle), and a prototype food package (right)

Self-repair of a scratch

Optical microscope images (height 0.50 mm, width 0.62mm) of the self-repairing process of the gas barrier layer scratched (left: just after being scratched, center: after being left for 60 minutes in humid air, right: after drying at 50 degree centigrade for 36 hrs)

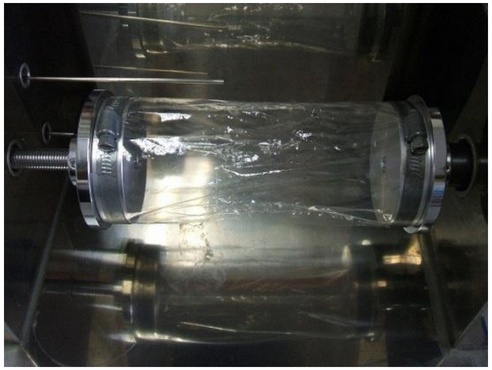
Oxygen gas barrier

3.4 【cc/m^2·day·atm】

0.98 【cc/m^2·day·atm】

Gelbo flex test

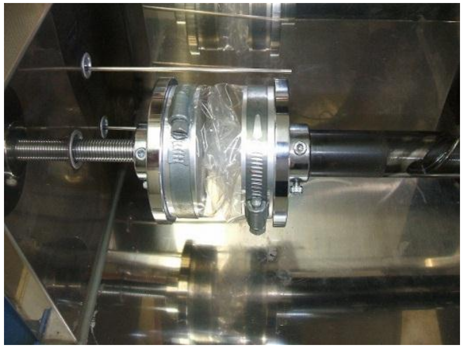
Equipment set up



Transparent vacuum deposited film
(after 20 times distortion)

Stretched

Repetition



Maximum distortion

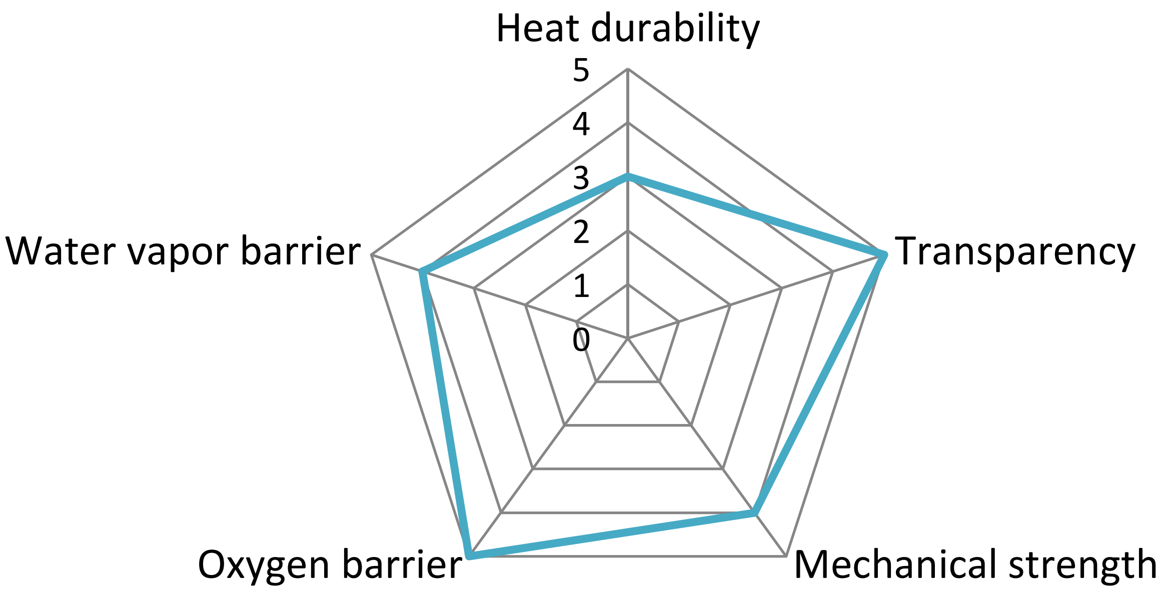
Oxygen permeability after gelbo flex test ($cm^3/m^2 \cdot day \cdot atm$)

【$cc/m^2 \cdot day \cdot atm$】

Number of bending	Commercial vacuum-deposited film	Commercial gas barrier layer coated film	Developed film
0	0.51	0.34	0.12
10	4.3	2.8	0.53
100	12	5.8	1.8

These figures are of laminated film with 25 micrometer thick polypropylene film. The gelbo flex tests were conducted under 23 degree centigrade and 65 percent related humidity. The oxygen permeation tests were conducted at room temperature and dry condition.

E.Water vapor barrier coating

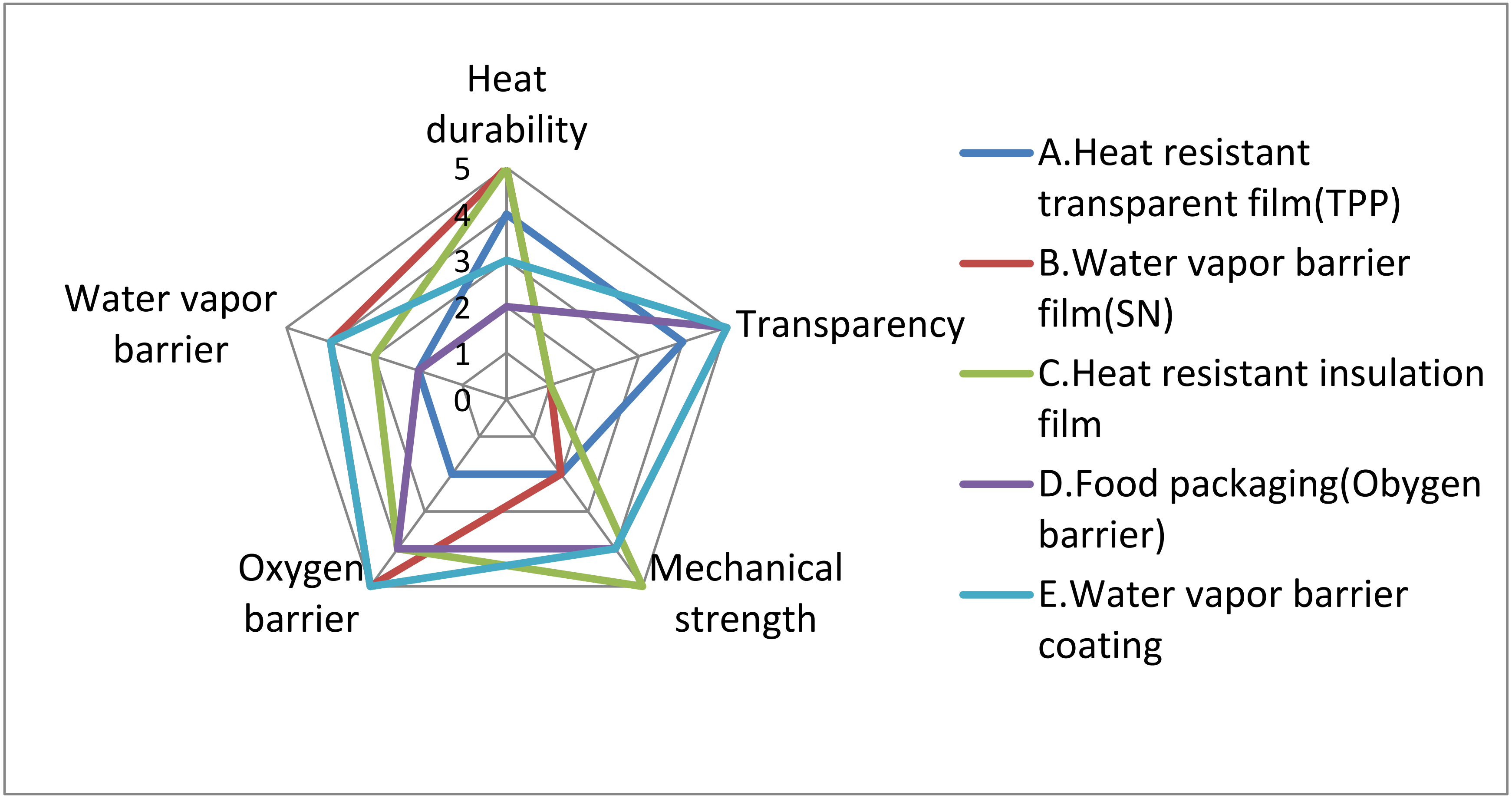


Water vapor barrier coating

1. Use synthetic smectite with high aspect ratio (>2000)
2. Exchange the interlayer cation from Na to ammonium.
3. Remove excess ion from the dispersion(<8ppm)
4. Apply the paste on PEN film with the wet thickness at approximately 0.3 micrometer
5. Heat at 180℃.
6. Realize high water vapor barrier at 6×10^{-3} g/m^2 day[1)], and 6×10^{-5} g/m^2 day[2)]

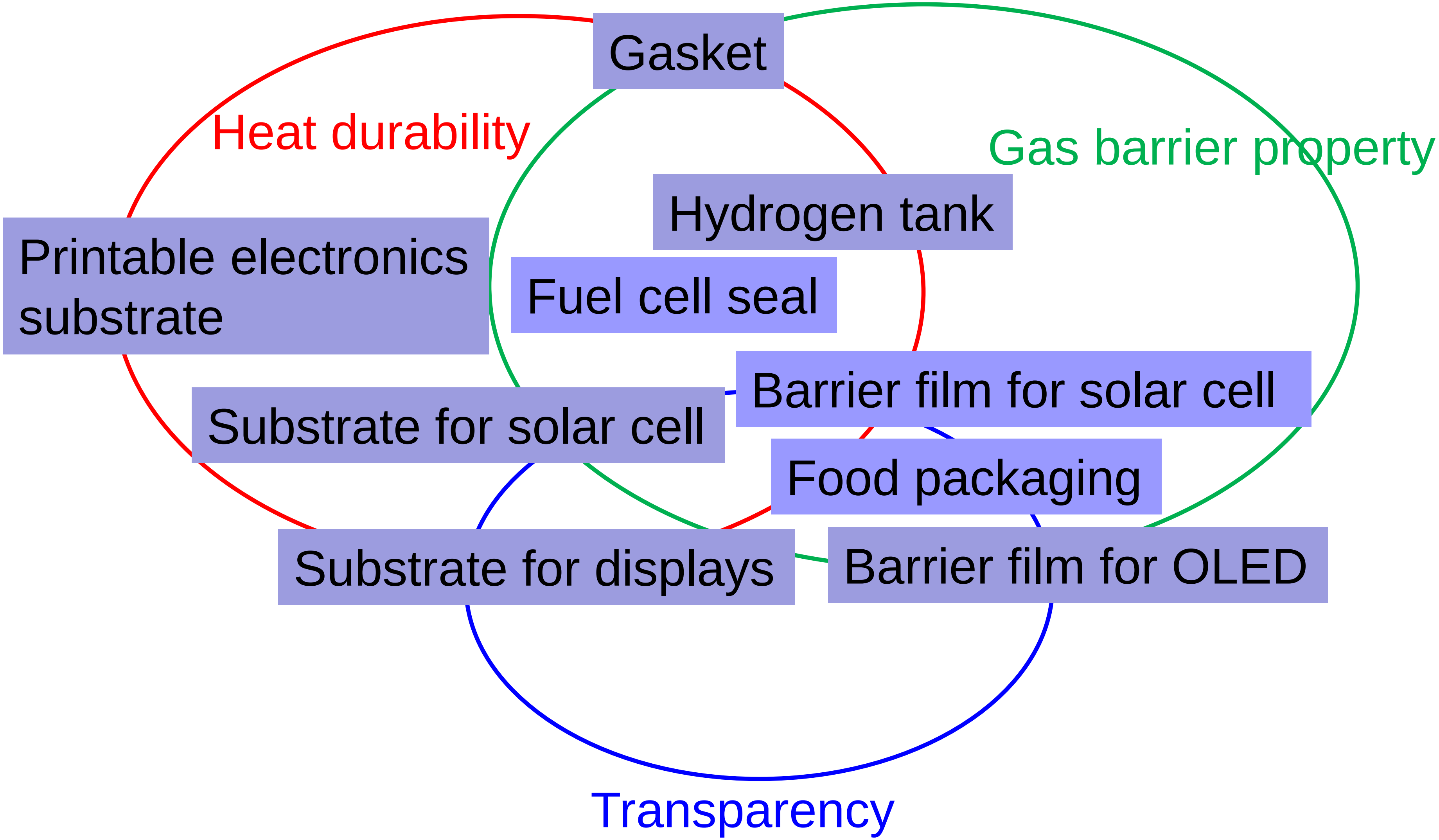
1) H. Tanaka, The 5th Clayteam Seminar, May.16, 2011, Tokyo
2) Japanese Patent No. 2011-213111

Film properties: Summary



Applications

Application map



Material design

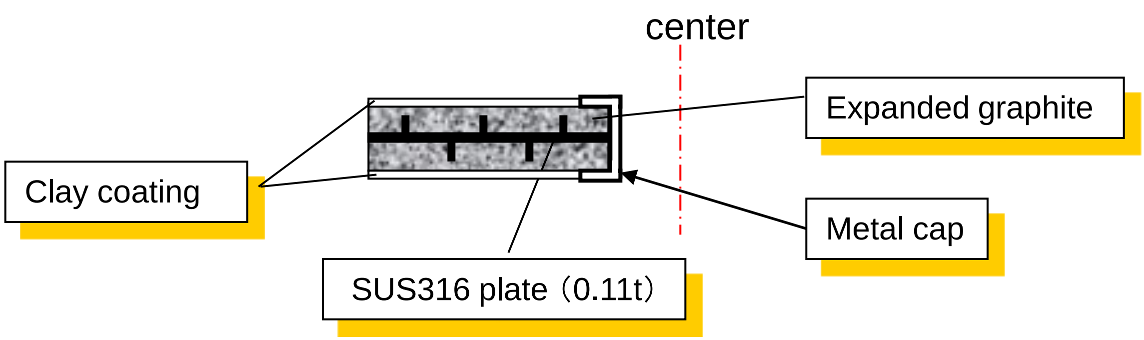
Properties must, want
Object
Limitation of process

Design

- Self standing or coating →heat durability
- Natural clay or synthetic clay→transparency
- Clay loading→flexibility
- Multilayer→Function separation
- Solid ratio, viscosity→production process

Anti-stick graphite gasket

Structure EXPANDED GRAPHITE /CLAY GASKETING SHEET



Cross section of the gasket

Advantage

- Non asbestos
- Highly heat-resistant
- Long life
-Good for wide variety of liquids and gas
-Excellent “anti-stick” surface

http://www.japanmatex.co.jp/

Current structural concepts of lightweight hydrogen tank

- Hydrogen Gas Barrier Liners Using Aluminum / Polymer Liners

  / Super Pressure Hydrogen Gas Tank for Automobiles (700 Bars) in Combination with Filament Winding

- Issues of Cryogenic Hydrogen Tanks for Aerospace Application

- All plastic gas tank is favorable because of its light-weight.

Super Pressure Hydrogen Gas Tank Using Liquid Polymer Liner

(Fuji Heavy Industries. Ltd.)

~ One of the major design concerns is hydrogen gas permeability

Hydrogen gas permeability of different coupons

Coupons		Thickness $[mm]$	Permeability $[\times 10^{-16} mol \cdot m / m^2 \cdot s \cdot Pa]$
CFRP (PYLOFIL#380)		1.061	0.529
Claist	ST	0.09	0.0009
	HR	0.073	0.0046
Claist Compound	ST	1.176	0.0078
CFRP (PYLOFIL#380)	HR	1.174	0.0035
Hydrogen Fuel Hose	(Reference 7)	-	33.49
Liquid Crystal Polyesters Resin	(Reference 8)	-	0.625
Virgin IM7/977-2/AF-191	(Reference 9)	-	0.4

*Eval Resin (Kuraray Co. Ltd) 0.031

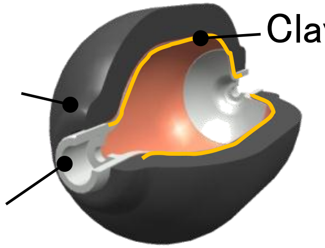
Yonemoto, K., Yamamoto, Y., Ebina, T. and Okuyama, K. (2008):. SAMPE’08.

CFRP Hydrogen tank using clay film as a gas barrier liner

CFRP core

Hand-layupped clay layer

CFRP filament winding

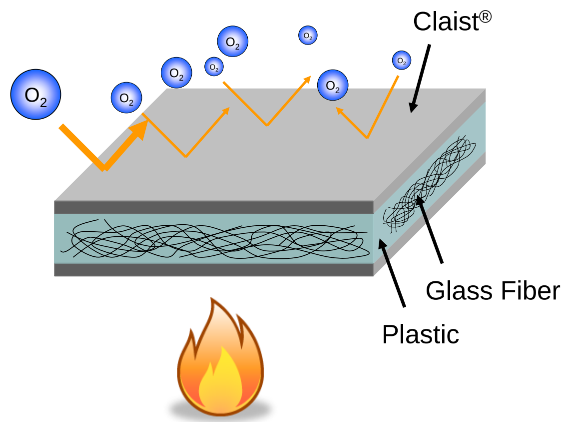


Structure of the clay film/CFRP hydrogen tank
Estimated broken pressure :70MPa

27L tank

Yonemoto, K., Yamamoto, Y., Ebina, T. and Okuyama, K. (2008):. SAMPE'08.

Transparent non-combustive sheet

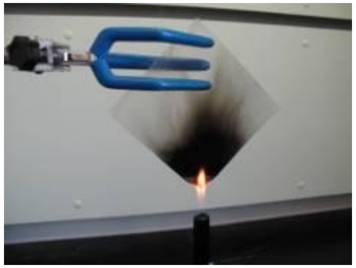


Proposed applications

Air deflector for vehicles with flexible solar cell

LED light
Kajiwara Electric Co

Control



with Clay film coating

Simple firing test

New building for transparent material development; September 2011

AIST Press release "Successful development of evolutional clay film products" , September 13, 2010

Fabrication of flexible organic light emitting diodes

ITO is treated at 300℃
$\rightarrow 4 \times 10^{-4}\,\Omega\mathrm{cm}$
rf magnetron sputtering

High gas barrier

High heat resistance

Fabrication of flexible OLED

The performance of the OLED is comparable to that of glass-base device.

- Turn on voltage 7.2V
- Luminous efficiency 2.7cd A^{-1}
- Electroluminescence peak at 530nm

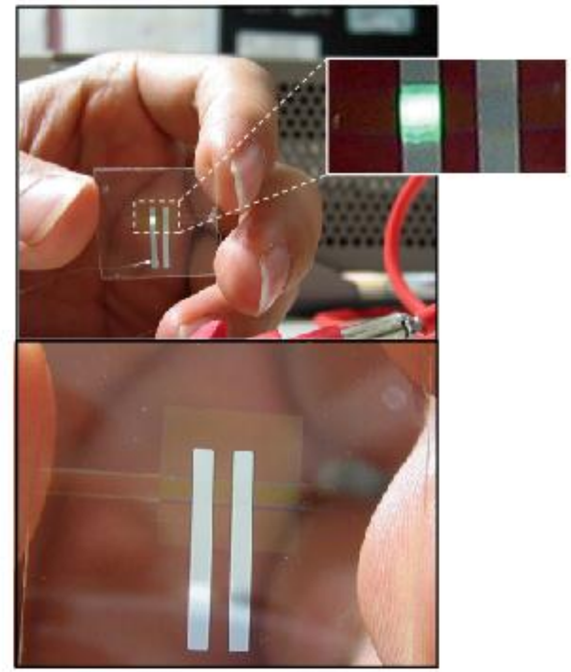
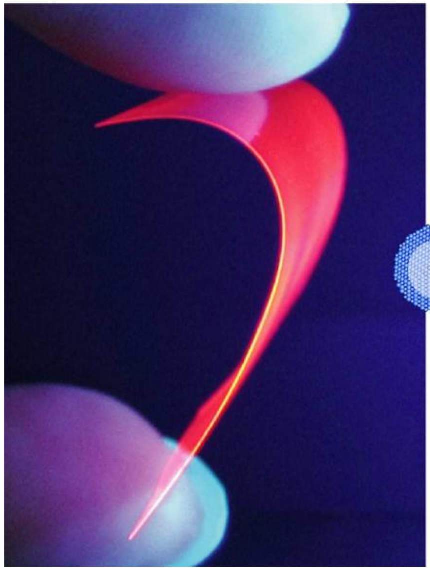
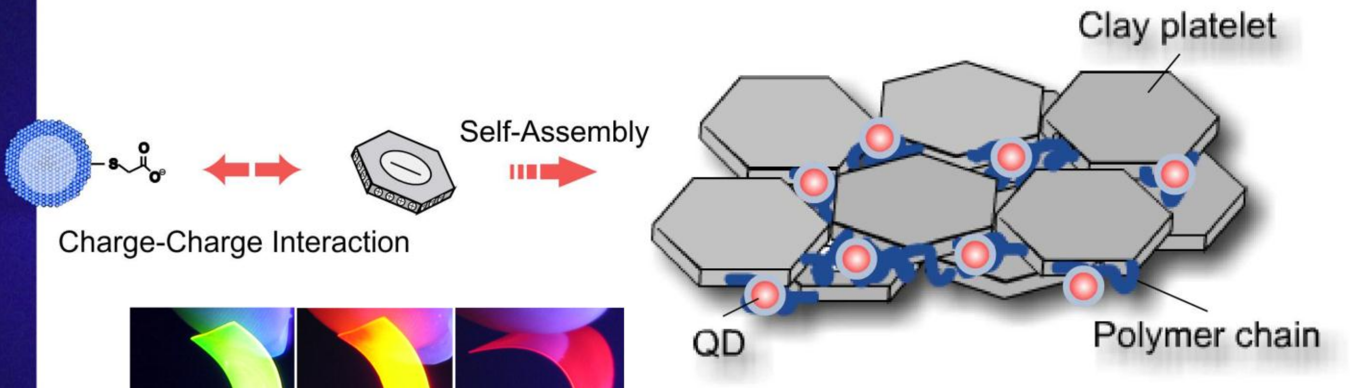


Fig. Digital camera image of a working device with one of two pixels switched on.

H. Tetsuka et al., Nanotechnology, 18 355701 (2007).
H. Tetsuka et al., J. Mat. Chem., 17, 3545-3550 (2007).

Quantum dot photo luminescent device





Incorporation of hydrophilic nanocrystals into flexible and transparent clay host using charge-charge interaction between nanocrystal surface and clay platelet.

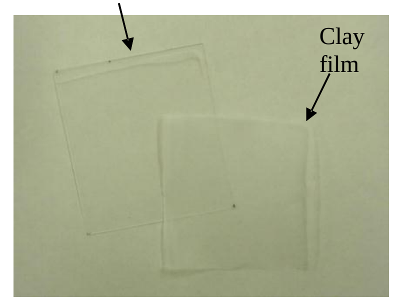
Tetsuka, H., Ebina, T. and Mizukami, F. (2008): Adv. Mater., 20, 3039-3043.

Towards the development of flexible optoelectronic devices

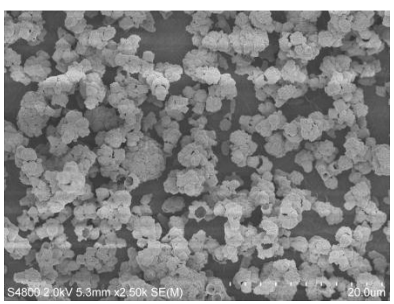
Dr. S. Venkatachalm

Preparation of clay film on glass substrate → Annealed at 60°C for 1h →

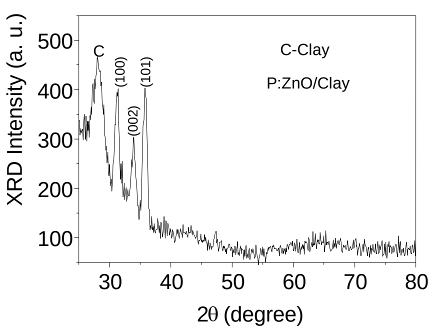
→



Preparation of ZnO thin film

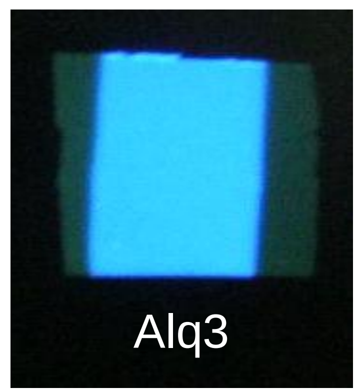


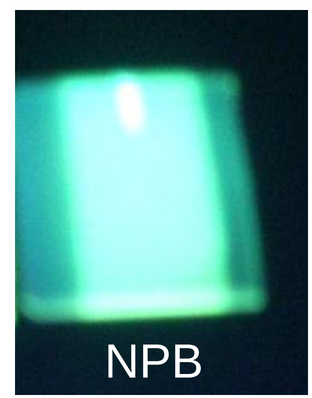
High magnification SEM images of ZnO thin films on clay substrate.



XRD patterns of ZnO thin film on clay substrate.

Preparation of electron (Alq3) and hole transport (NPB) layer:



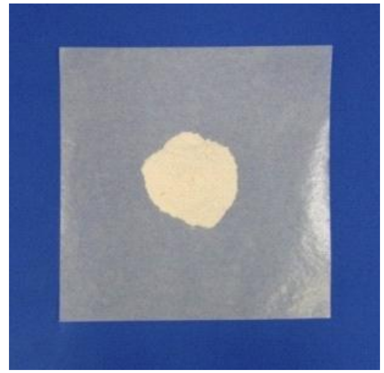


Photographs of light emission under UV light (365 nm)

Clay synthesis from rice husk

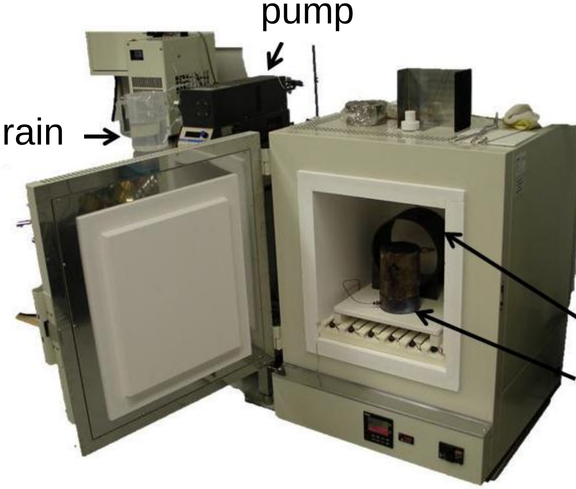
Rice husk

1. Combustion
2. Add Mg and Na
3. Hydrothermal treatment



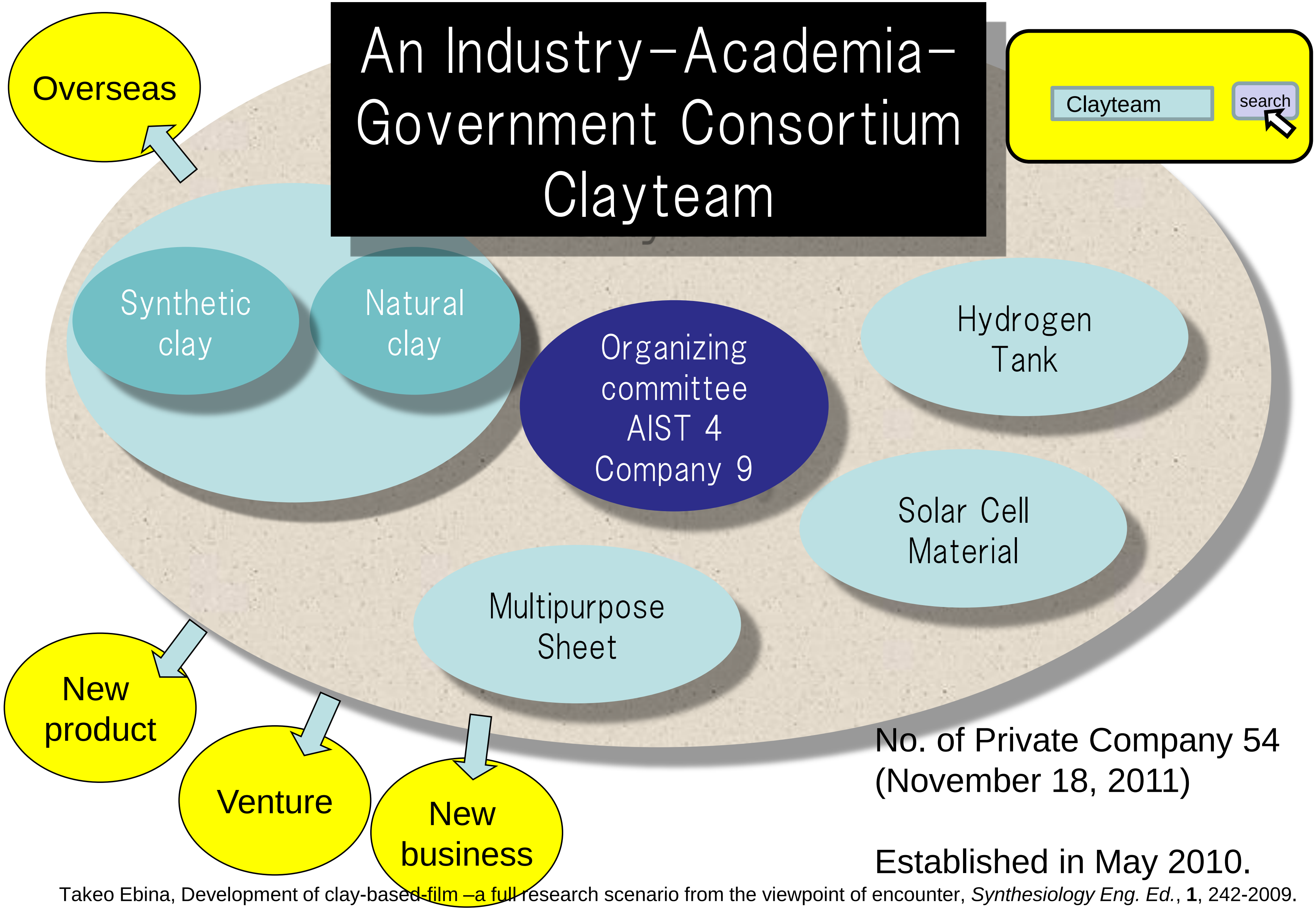
Synthetic clay

Transparent film made from rice husk



Reaction apparatus for excess heated water vapor reaction

An Industry-Academia-Government Consortium Clayteam



No. of Private Company 54 (November 18, 2011)

Established in May 2010.

Takeo Ebina, Development of clay-based-film –a full research scenario from the viewpoint of encounter, *Synthesiology Eng. Ed.*, **1**, 242-2009.

Summary

Clay-based flexible film has excellent performance in thermal stability, gas barrier property, and so on.

Different types of films including transparent types have been developed to suit different applications.

Development of products using this material on various applications will contribute to establish the sustainable society.

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