New Transparent High-Barrier Film for Advanced Retort Applications

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ABSTRACT

"KURARISTER™", which is henceforth called **"Hybrid film",** is a new transparent high-barrier film for advanced retort applications, and which is a biaxial oriented polyethylene terephthalate (PET) film or a biaxial oriented polyamide (PA) film with a hybrid composite coating on both sides. The hybrid film shows excellent gas barrier properties before and after sterilization that don't depend on humidity, sterilization conditions, or the structure of the laminated film. As the hybrid composite coating layer has excellent scratch resistance and flex resistance, the gas barrier properties are stable during converting, transportation storage, flexing and tension etc.

INTRODUCTION

Packages for sterilized food have traditionally been metal cans, glass bottles and aluminum foil pouches. Recent developments of pouch structures including transparent plastic barrier films are expected to show growth as replacements for the older materials thanks to their improved properties as "Microwave-ability", "Metal Detection Capability", and "Reduction of incinerated residue"[1,2,3]. Against this background, a new hybrid, transparent high-barrier film **"Hybrid film"** [4,5] has been developed to meet the requirements of these applications and is already being produced on a commercial scale.

Hybrid film shows features, including (a) very high and consistent oxygen barrier before, during and after retort, (b) oxygen barrier performance independent of the retort method, (c) barrier not affected by humidity, elongation (5%), scratching or flexing, (d) high transparency: similar to PET or PA substrates, (e) easy printing without surface pre-treatment, (d) easy handling: no curling, low coefficient of friction. In this paper these features of hybrid film are described based on evaluation results.

EXPERIMENTAL

The laminated films were prepared with "PET based barrier film / ad / PA film / ad / CPP" and "PA based barrier film / ad / CPP" structures.　Major properties such as oxygen gas barrier and mechanical properties before / after retort treatment were examined.　Detailed experimental materials and test methods are described in Appendix 1.

RESULTS AND DISCUSSION

1. Mechanical properties

Mechanical properties of both a PET based hybrid film and a PA based hybrid film are summarized in Table 1. Tensile strength at break of both hybrid films was slightly weaker than substrate films. Elongation at break of both hybrid films was the same as substrate films. Tensile modulus of both hybrid films was a little higher than substrate films. The puncture resistance and impact strength of PA based hybrid film was 80 to 90% of PA film, however the values are of a sufficient high level to keep the features of PA based film. Total light transmission of both hybrid films was the same as PET film. In a final comparison, features of the product regarding mechanical properties were almost equal to the substrate films.

When PA film is used as the surface layer of a laminated film, mechanical properties of PA film deteriorate during retort by an oxidation reaction. PA based hybrid film is expected to be used in a two layer laminate structure, which is PA based hybrid film // CPP, for retort applications. So, mechanical properties of the two layer laminated film were evaluated before and after retort treatment. For comparison, PA film // CPP was evaluated, too. The results are summarized in table 2. Mechanical properties of PA film // CPP deteriorate, especially impact strength were down to 30% of the before retort levels. On the other hand, in case of PA based hybrid film, mechanical properties after retort were almost equal to those before retort. This good result was attributed to protection of the PA film by the hybrid composition layer.

2. Oxygen gas barrier properties.

The Oxygen Transmission Rate (OTR) for laminated films before and after retort is listed in Table 3. OTR results of PET based hybrid film were 0.4cc/m^2/day/atm, and don't depend on retort methods, retort temperature or retort time. In the case of a PA based hybrid film, OTR after retort, under conditions of hot water retort, 120°C, 30minutes, was 0.7cc/m^2/day/atm even in the worst case. The relationship between humidity and OTR is shown in Fig.1. OTR is independent of humidity. Concerning PET based inorganic coated film, OTR results were 0.3 to 1.5 cc/m^2/day/atm with some scatter. These values were dependent on sterilization conditions.

3. Peel strength of laminated film after retort

In Table 4 results regarding peel strength of laminated film including hybrid film are summarized. All peel strength results were more than 400g/15mm which is considered sufficient for most retort applications. It was found that peel strength can be improved by choosing a suitable adhesive for hybrid film.

4. Properties related with converting

The wetting index of PET based hybrid film and PA based hybrid film was at the same level as each corona treated PET film and corona treated PA film. According to printing test results by customers, both solvent based ink and water based ink could be directly applied to hybrid films by gravure rolls without difficulty. Coefficient of static friction (COF) levels of both PET based hybrid film and PA based hybrid film were similar to PET film. As shown in Figure 2 the COF of hybrid film doesn't depend on humidity and temperature. The COF is low both between hybrid film and hybrid film and between hybrid film and a metal roll. This means easy handling of hybrid film without generating wrinkles during printing and laminating.

5. OTR after abuse test

5% elongation and scratch tests were studied as an indication of abuse resistance. Deterioration of oxygen barrier properties by 5% elongation and gelbo flexing testing was very small as shown in table 6 and Figure 3. Because the matrix phase of the hybrid composition is a polymer with stretchable properties, it was expected that small deformation of the hybrid film would hardly affect gas barrier properties. The hybrid films showed excellent scratch resistance thanks to a strong interaction between polymer and inorganic compounds in the hybrid composition. Furthermore, both side barrier coating of the hybrid film improved reliability of gas barrier properties after abuse tests. In the case of inorganic coated film, scratch resistance and abrasion resistance were not as good due to very thin thickness of the coating layer.

CONCLUSIONS

1. Hybrid films consistently show excellent oxygen barrier properties before and after sterilization. The oxygen barrier property does not depend on humidity, or sterilization conditions.
2. Hybrid film has good flex, scratch and 5% elongation resistance thanks to a stretchable polymer matrix phase in the hybrid composition and strong interaction between the polymer and inorganic materials.
3. PA based hybrid film shows good mechanical properties such as impact strength, puncture resistance… etc even after sterilization, because the PA substrate is protected by a hybrid composition layer from oxidation reaction during retort.
4. Thanks to similar COF and wetting index properties of the hybrid film with PET film, handling during printing and laminating is easy.

ACKOWLEDGMENTS

The authors are grateful to the people that support preparing this paper, especially those in EVAL COMPANY of America.

REFERENCES

1. Japan Canners Association The Canners Journal, Vol.85, No.8, p733-755(2006)
2. K. Kobayashi Journal of Packaging Science & Technology Japan, Vol.9, No.6, p345-349(2000)
3. T. Katsura PACKPIA, September,p40-45(2000)
4. T. Oshita, Journal of Packaging Science & Technology Japan, Vol.15, No.4, p185-190(2006)
5. T. Oshita, Convertech, No.402, p92-94(2006)

Table 1 Mechanical properties of hybrid film

Measurement[1)] Items		Units	PET based hybrid film	PA based hybrid film	PET film	PA film
Tensile strength at break	MD	MPa	180	190	250	220
	TD		150	190	230	260
Elongation at break	MD	%	120	80	110	91
	TD		170	87	130	100
Tensile modulus	MD	GPa	4.7	3.7	4.8	2.4
	TD		4.3	3.6	4.7	2.2
Puncture resistance		N	-	7.2	-	9.3
Impact strength		J	-	0.69	-	0.79
Total light transmission		%	93.0	92.5	89.9	91.9

1) Measurement conditions: 23ºC, 50%RH

Table 2 Mechanical properties of laminated film

Measurement[1)] Items		Units	PA based hybrid film //CPP film		PA film // CPP	
			Before retort	After retort[2)]	Before retort	After retort[2)]
Tensile strength at break	MD	MPa	63	65	65	41
	TD		60	55	65	39
Elongation at break	MD	%	83	90	100	40
	TD		93	82	100	40
Tensile modulus	MD	GPa	1.3	1.1	0.99	0.80
	TD		1.2	1.0	0.96	0.65
Puncture resistance		N	8.5	8.6	10.0	6.9
Impact strength		J	0.98	1.1	1.2	0.36

1) Measurement condition: 23ºC, 50%RH
2) Retort condition: Hot water retort, 120ºC, 30min

Table 3 Oxygen transmission rate (OTR) of laminated film after retort

Retort condition (Retort method / Temp. / Time)	OTR(cc/m^2/day/atm)[3)]		
	PET based Hybrid film [(1)]	PA based Hybrid film[(2)]	PET based inorganic coated film[(1)]

Before retort	0.4	0.6	0.3
Hot water retort / 120ºC / 30min	0.4	0.7	0.6 - 1.1
Hot water retort / 120ºC / 60min	0.4	-	0.9 – 1.2
Hot water retort / 120ºC / 180min	0.4	-	0.9 -1.2
Hot water retort / 135ºC / 30min	0.4	-	1.1
Spray retort / 120ºC / 30min	0.4	-	1.0
Spray retort / 135ºC / 30min	0.4	-	1.0
Steam retort / 120ºC / 30min	0.5	-	0.5 – 1.5

1) Structure of the laminated film: PET based gas barrier film // PA film $_{15}$// CPP $_{50}$
2) Structure of the laminated film: PA based gas barrier film // CPP $_{50}$
3) OTR measurement condition: 20ºC, 85%RH / 100%RH

Table 4 Peel strength of laminated film after retort

Retort condition (Retort method / Temp. / Time)	Peel strength (g/15mm) [3]		
	PET based Hybrid film [1]	PA based Hybrid film [2]	PET based inorganic coated film [1]
Before retort	550	500	250 - 300
Hot water retort / 120ºC / 30min	520	540	250 - 300
Hot water retort / 120ºC / 60min	480	-	250 - 300
Hot water retort / 120ºC / 180min	500	-	-

1) Structure of the laminated film: PET based gas barrier film // PA film $_{15}$// CPP $_{50}$
2) Structure of the laminated film: PA based gas barrier film // CPP $_{50}$
3) Peel strength measurement condition: 23ºC, 50%RH, 3hours later after retort

Table 5 Properties related with converting

Measurement[1] Items	PET based hybrid film	PET film (corona treated)	PA based hybrid film	PA film (corona treated)
Wetting index	>54	>54	>54	50
Coefficient of static friction	0.45	0.58	0.47	1.11

1) Measurement conditions：23ºC, 50%RH

Table 6 Oxygen transmission rate (OTR) after abuse test

Abuse test	OTR(cc/m^2/day/atm)[1]	
	PET based Hybrid film	PET based Inorganic coated film
Before abuse test	0.3	0.3
5% elongation test	0.4	0.8
Scratch test	0.4	40<

1) OTR measurement conditions：20ºC, 85%RH / 85%RH

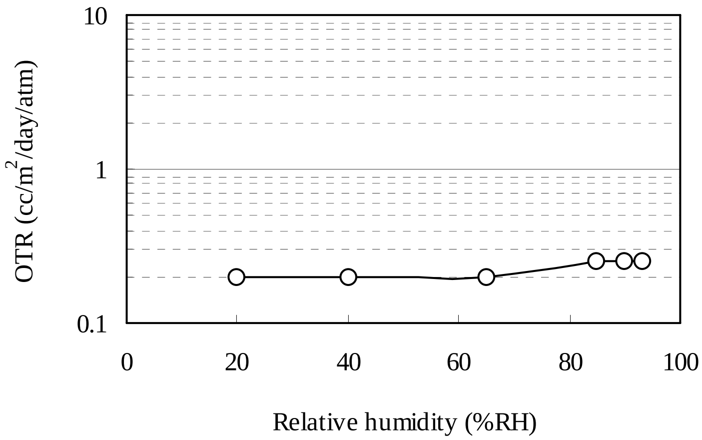

Fig. 1 Relationship between humidity and OTR[1)]

1) OTR measurement temperature: 20ºC

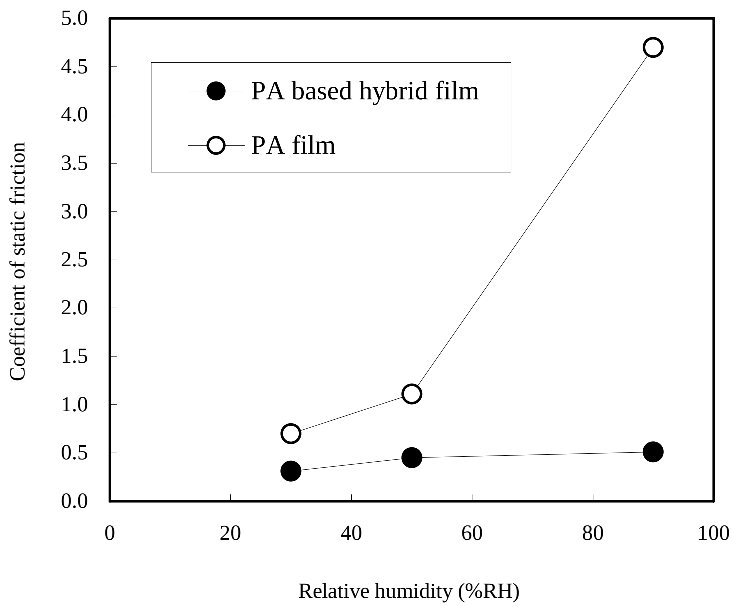

Fig. 2 Coefficient of static friction vs Relative humidity

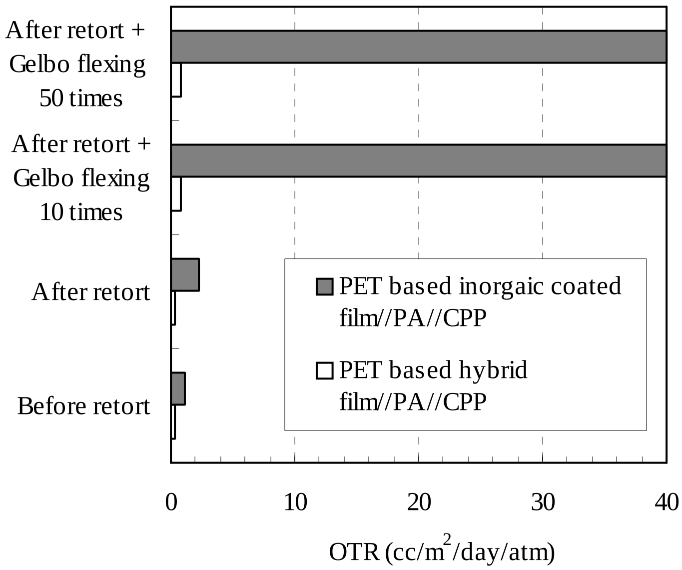

Fig.3 OTR[1)] of laminated film after retort and gelbo flexing test

1) OTR measurement condition: 20ºC, 85%RH / 100%RH

Appendix 1

Materials

1. **"KURARISTER™"**, which is henceforth called "Hybrid film", is a biaxial oriented PET film or a biaxial oriented PA film with hybrid composite coating on both sides. The hybrid composite is composed of a polymer and an inorganic component.
2. Grade of biaxial oriented polyamide (PA) film as a layer of laminated film is EMBLEM ONBC 15 produced by UNITIKA CO., LTD.
3. Grade of cast polypropylene (CPP) film as sealant of laminated film is RXC-18 produced by TOHCELLO CO., LTD.
4. Grade of adhesive (AD) for laminated film is Takelac A-385 and Takenate A-50 produced by MITSUI CHEMICALS POLYURETHANES, INC.
5. Inorganic coated PET film was used for comparison.
6. Structure of laminated film including PET based barrier film is PET based barrier film / ad / PA film / ad / CPP.
7. Structure of laminated film including PA based barrier film is PA based barrier film / ad / CPP.

Test methods

(1) Oxygen barrier property before sterilization

In this test, oxygen transmission rate (OTR) of a barrier film itself or a laminated film including a barrier film is measured under the below condition.

Equipment: MOCON10/50, Condition of OTR: 20°C, 85%RH (Oxygen provided side) / 85%RH (Oxygen detected side)

(2) Oxygen barrier property after sterilization

A pouch was made from two laminated films including a barrier film and was filled with water. The pouch was sterilized under specific conditions. After sterilization, laminated film samples were cut from the pouch. Water on the surface of the laminated film was removed by paper and OTR was measured under the below conditions.

Equipment: MOCON10/50, Condition of OTR: 20°C, 85%RH (Oxygen provided side) / 100%RH (Oxygen detected side)

(3) Tensile strength at break, tensile elongation at break and tensile modulus

Equipment: "AUTOGRAPH AGS-H" (SHIMAZU CORPORATION), Measurement condition: 23°C, 50%RH, tensile speed in case of tensile strength at break and tensile elongation at break: 200mm/minute, tensile speed in case of tensile modulus: 50mm/minute

(4) Puncture resistance

Equipment: "AUTOGRAPH AGS-H" (SHIMAZU CORPORATION), Measurement condition: 23°C, 50%RH, puncture speed: 50mm/minute, diameter of needle tip: 1mm

(5) Impact strength

Equipment: "Film Impact Tester" (Toyo Seiki Seisaku-sho, LTD.), Measurement condition: 23°C, 50%RH,

(6) Total light transmission

Equipment: "Spectro color meter NF902" (Nippon Denshoku Industries Co., Ltd.), Measurement condition: 23 °C, 50%RH

(7) Wetting index

Measurement by using reagent for wet index (Wako Pure Chemical Industries, Ltd.), Measurement condition: 23°C, 50%RH

(8) Coefficient of static friction

Equipment: "Friction Angle Tester" (Toyo Seiki Seisaku-sho, LTD.), Measurement condition: 23°C, 50%RH,

(9) 5% elongation test

In 5% elongation test, barrier film is elongated to 5% by using a below equipment. And OTR of samples after elongation is measured. Equipment: handmade equipment with handle, Measurement condition: 23°C, 50%RH, tensile speed: about 100mm/minute

(10) Scratch test

In scratch test, back and forth motion of sandpaper on the barrier film by using a below equipment was repeated 5 times. And OTR of samples after scratch test is measured. Equipment: “Color Fastness Rubbing Tester” (TESTER SANGYO CO., LTD.), Measurement condition: 23^{o}C, 50%RH,

(11) Gelbo flexing test

In scratch test, laminated film including barrier film after sterilization is flexed by using below equipment. . And OTR of the laminated film after flexing is measured.

Equipment: “Gelbo flex tester” (Rigaku Kogyo), Measurement condition: 23^{o}C, 50%RH, number of gelbo flexing 10times, 50times

(12) Retort treatment

Equipment: Retort treatment machine “RCS”(HISAKA WORKS, LTD.), Measurement condition: 23^{o}C, 50%RH, www.tappiplace.org

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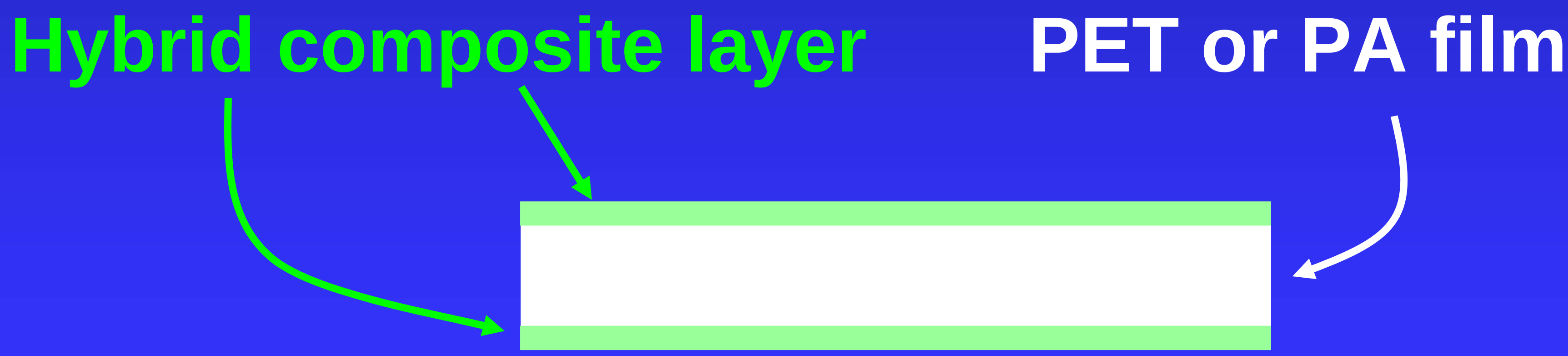
New Transparent High-Barrier Film for Advanced Retort Applications

“ KURARISTER™ ”

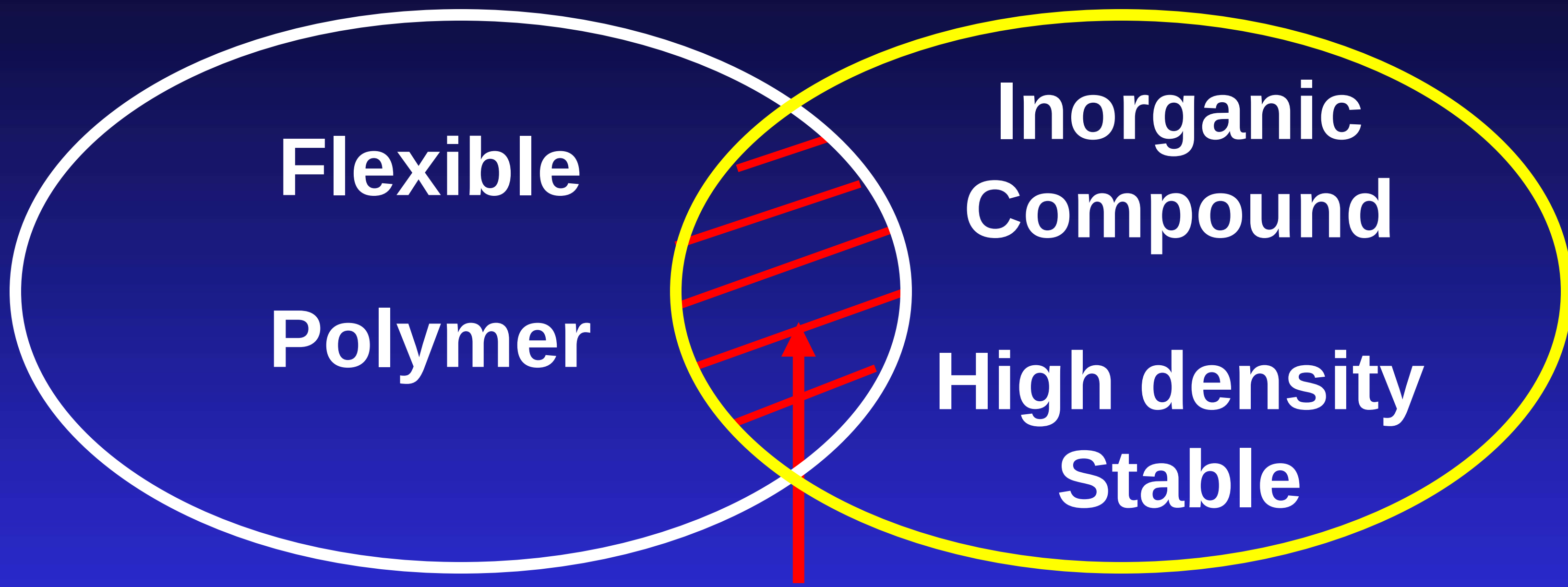
Presented by:
Tatsuya Oshita
Research Manager
KURARAY CO., LTD

Structure of Hybrid Film

- Hybrid composite with gas barrier property
- Both sides coating on a base film
- PET film or PA film



Hybrid Film



Strong interaction

Restricted polymer molecular movement

- ➢ Gas barrier properties

Polymer matrix

- ➢ Resistance to deformation as flexion etc.

Features of Hybrid Film

- Very high and consistent gas barrier before, during and after retort
- Gas barrier independent of retort conditions
- Gas barrier not affected by humidity, elongation, scratching or flex
- Easy printing without surface pre-treatment
- Easy handling: no curl, very low coefficient of friction (COF)

Oxygen Barrier With Varied Retort Conditions

Retort method	Retort conditions	OTR [3] ($cc/m^2/day/atm$)		
		PET based hybrid film[1]	PA based hybrid film [2]	PET based inorganic coated film [1]
Before retort		0.4	0.6	0.3
Hot water	120ºC/30min	0.4	0.7	0.6 – 1.1
Hot water	120ºC/180min	0.4	-	0.9 – 1.2
Hot water	135ºC/30min	0.4	-	1.1
Spray	135ºC/30min	0.4	-	1.0

(1) Sample: Barrier film // PA film15 // CPP film50

(2) Sample: Barrier film // CPP film50

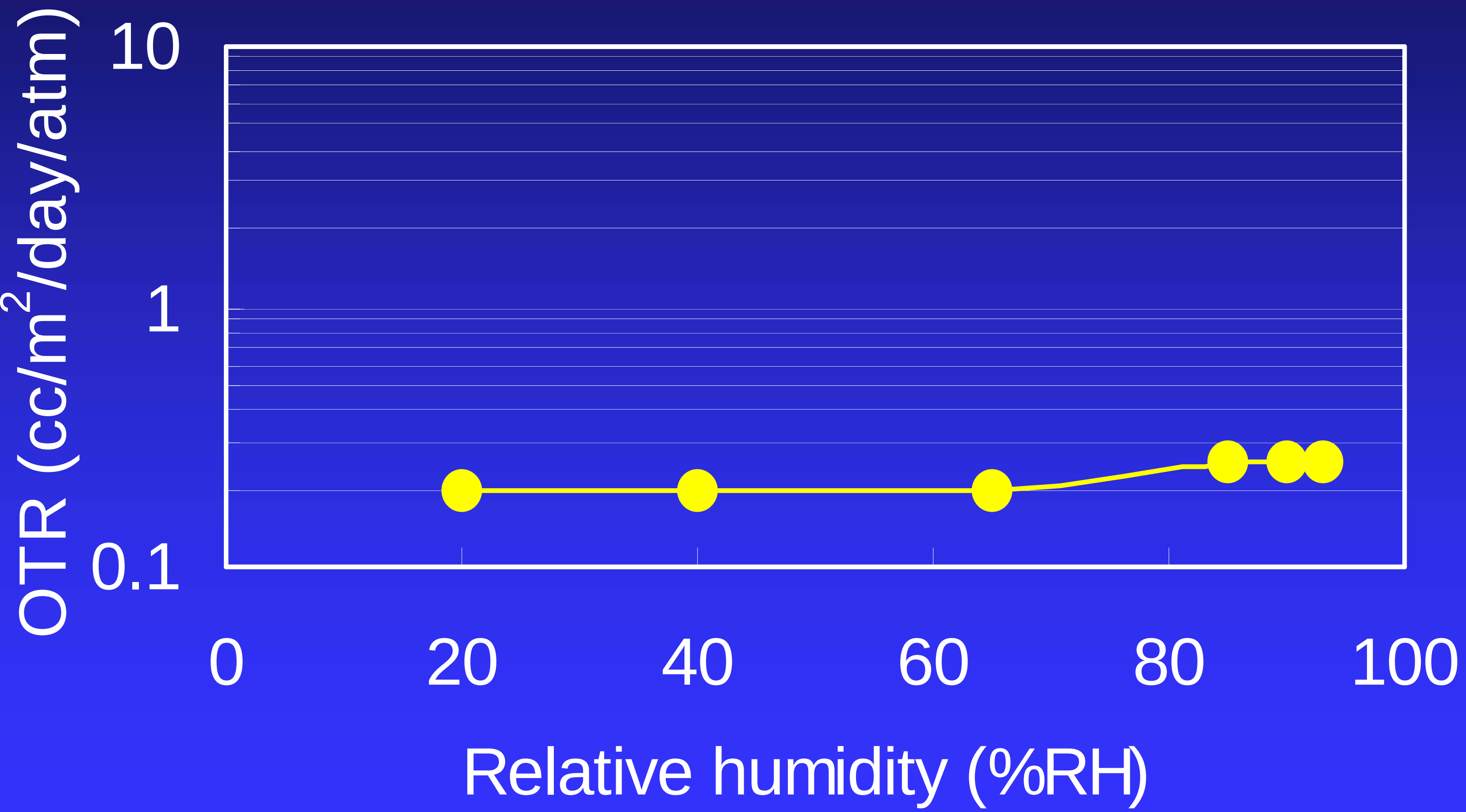
(3) OTR: 20ºC, 85%RH / 100%RH

Oxygen Barrier With Varied Retort Methods

Before or after Retort	OTR conditions	OTR (cc/m²/day/atm)		
		Hot water[(1)]	Spray [(1)]	Steam [(1)]
Before retort (coated film)	20ºC 85%RH	0.3	0.3	0.3
Before retort (laminated film)	20ºC 85/100%RH	0.4	0.4	0.4
After retort (laminated film)		0.4	0.4	0.5

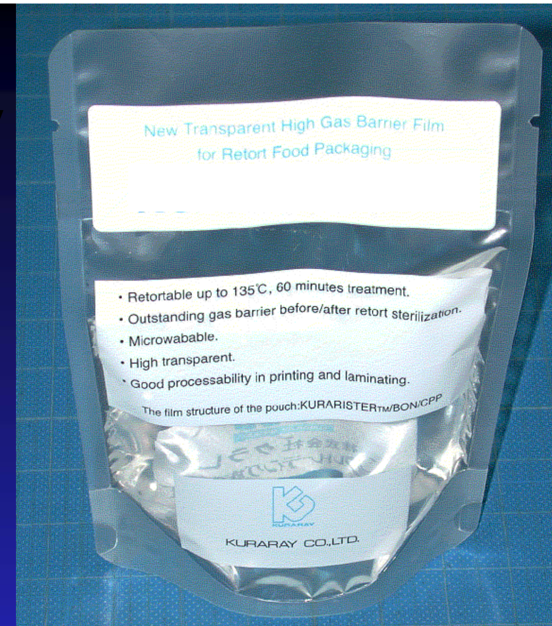
(1) Retort conditions: 120ºC, 30min.

OTR vs. Relative Humidity



Printability

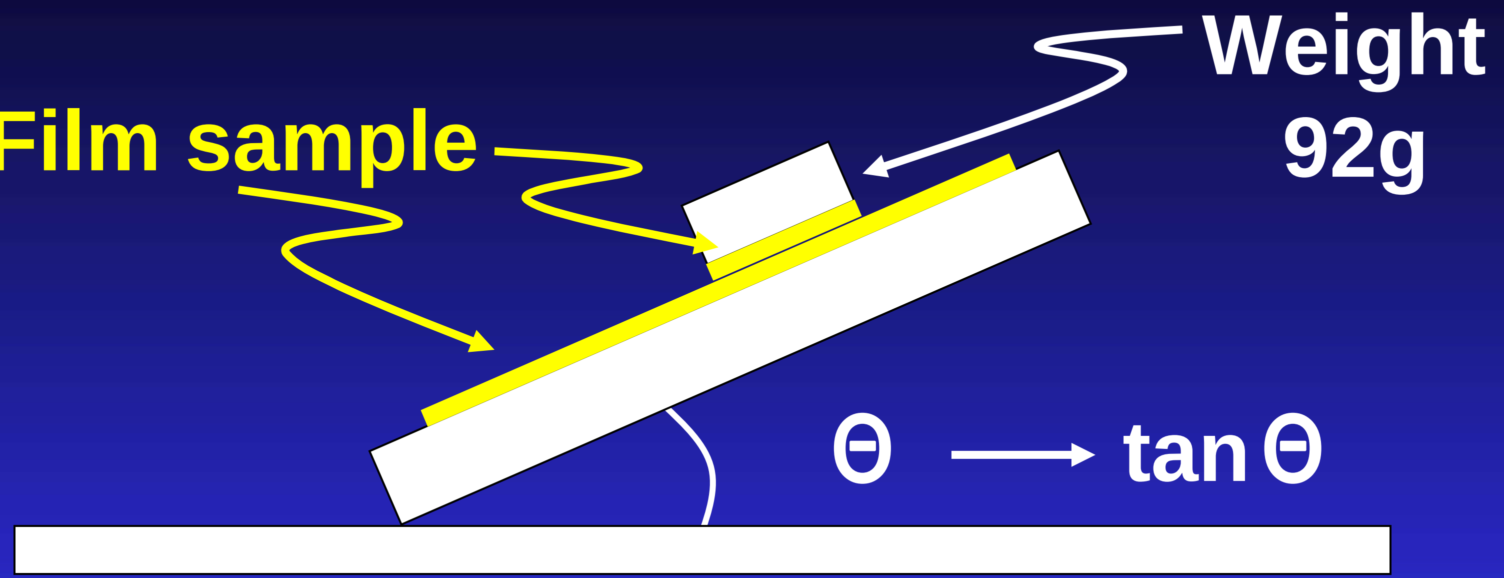
- Solvent based ink
- Water based ink



Hybrid film / Solvent based ink / Ad / PA film / Ad / CPP

Wetting index（dyne/cm）	
PET based hybrid film (no corona treatment)	PET film (corona treated)
>54	>54

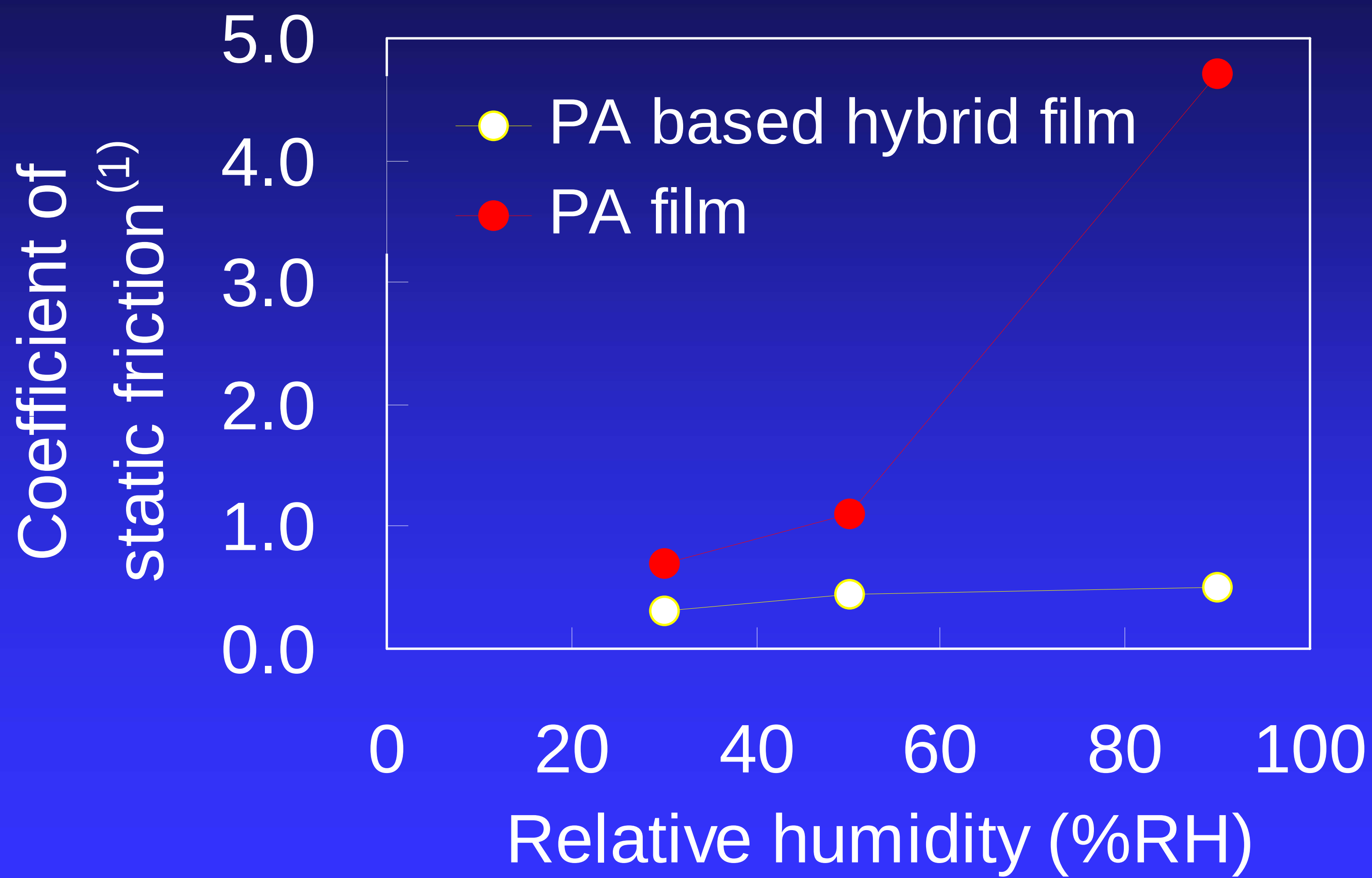
Coefficient of Static Friction



Coefficient of static friction[1]			
PET based hybrid film	PA based hybrid film	PET film	PA film
0.45	0.47	0.58	1.11

(1)Coefficient of static friction: 23ºC, 50%RH

Humidity-Dependence of Coefficient of Static Friction



(1) Temperature: 23ºC

Abuse in Production Process

Scratching/expanding

Converting

Folding/sealing

Pouch making

Expanding/sealing

Filling

Expanding/shrink

Retort

Hitting

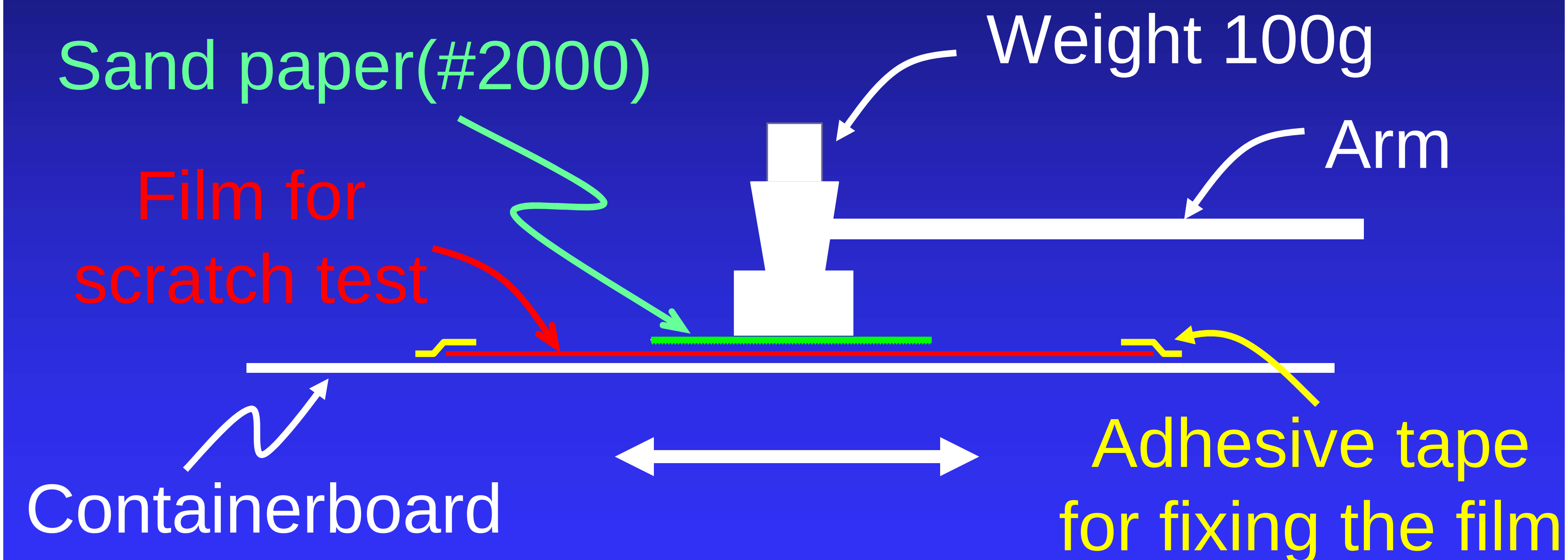
Transportation

Market

Scratch Resistance

Evaluation method

OTR after scratching 5 times on barrier layer



Back-and-forth motion of the containerboard with the film

OTR after Scratch Test

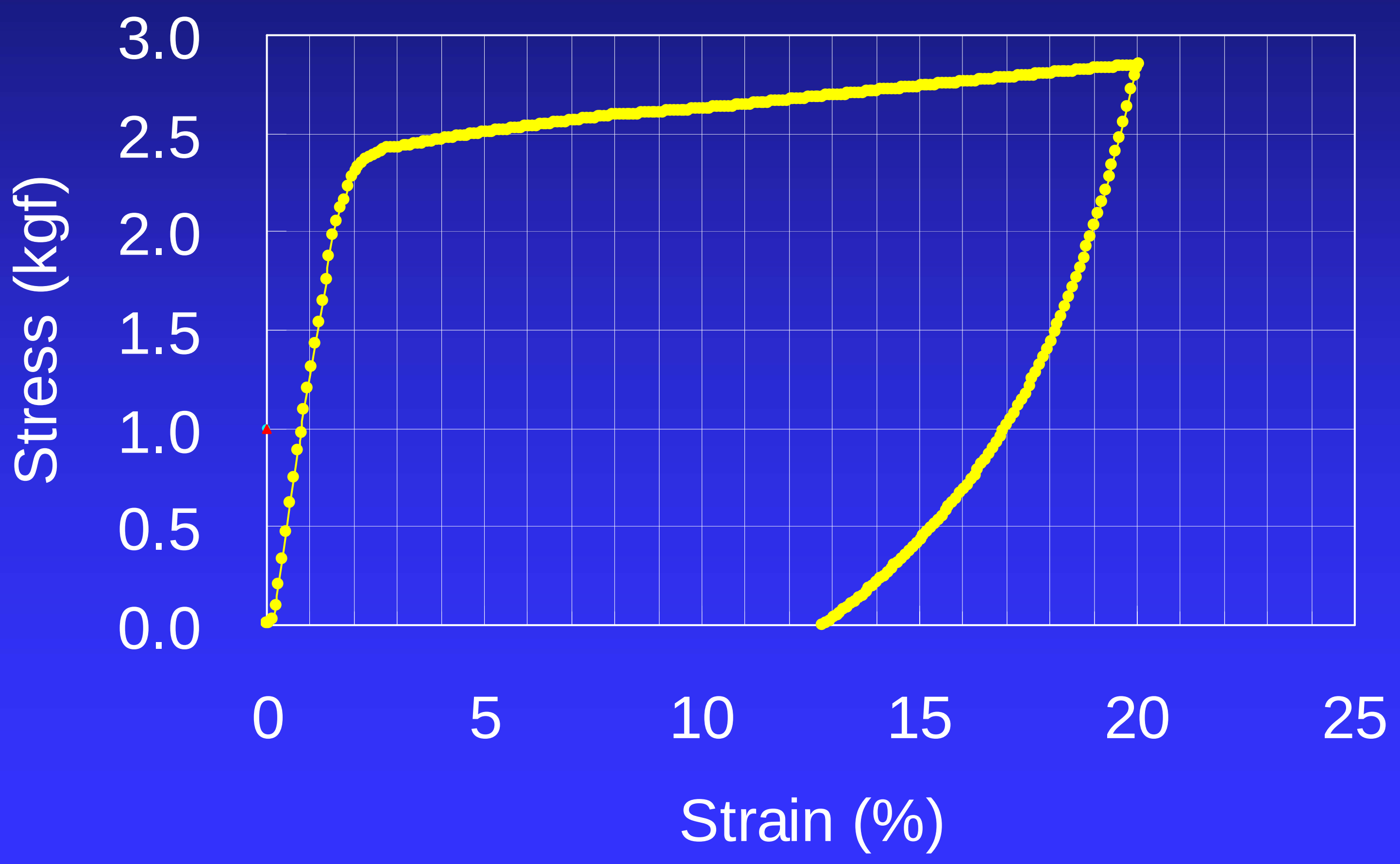
Scratch[1] times	OTR [2] (cc/m^2/day/atm)	
	PET based hybrid film	PET based Inorganic coated film
0 time	0.3	0.3
5 times	0.4	>40

(1) Scratch Conditions: 23ºC, 50%RH

(2) OTR: 20ºC, 85%RH / 85%RH

Stress-Strain Hysteresis Curve

- Plastic deformation in more than 3% strain

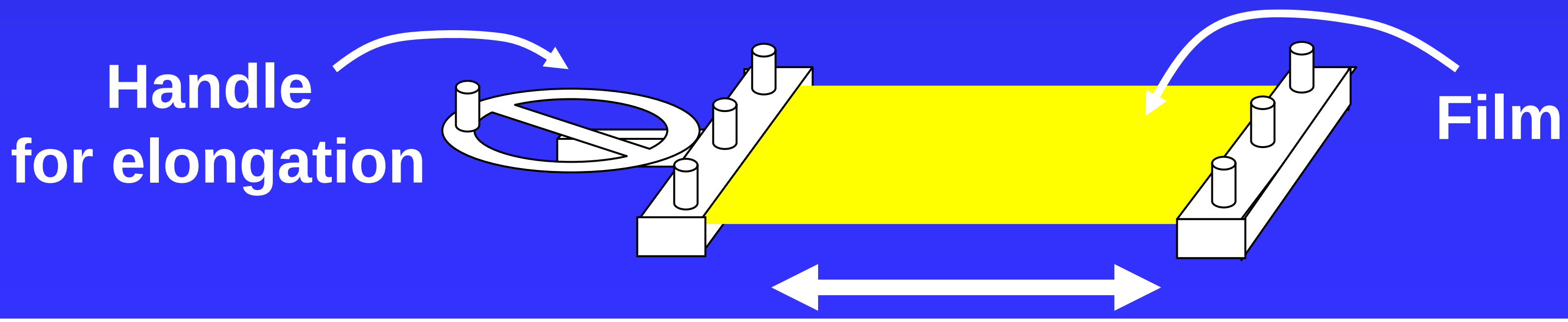


OTR after Elongation

Elongation(1) Ratio	OTR (2)(cc/m²/day/atm)	
	PET based hybrid film	PA based hybrid film
0%	0.3	0.5
5%	0.4	0.7

(1) Elongation: 23ºC, 50%RH, 100mm/min

(2) OTR: 20ºC, 85%RH / 85%RH



OTR after Folding & Retort

Pouch

120^{o}C
30min.

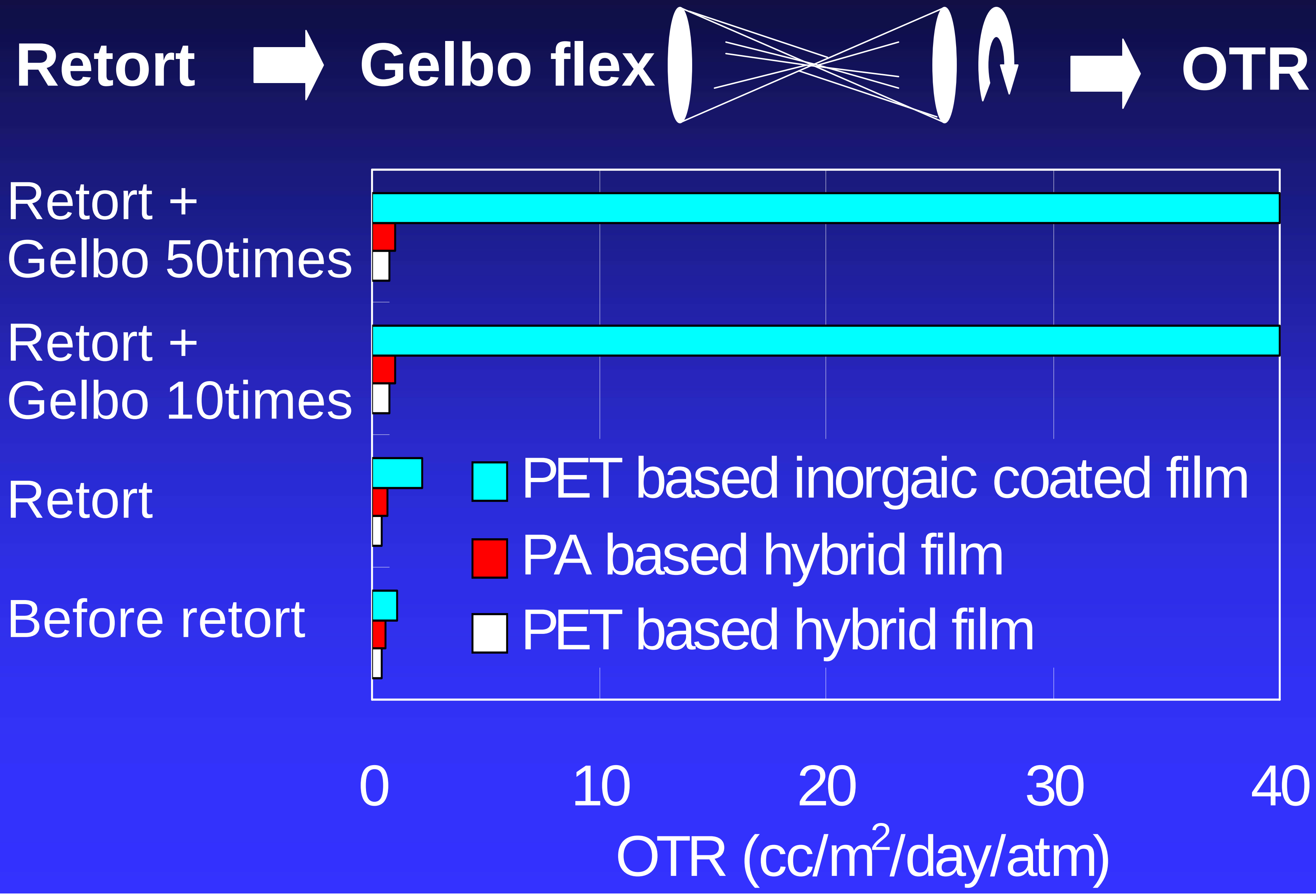
Laminated film

Folding

OTR [1](cc/m^2/day/atm)	
After folding & retort	After retort
0.4	0.4

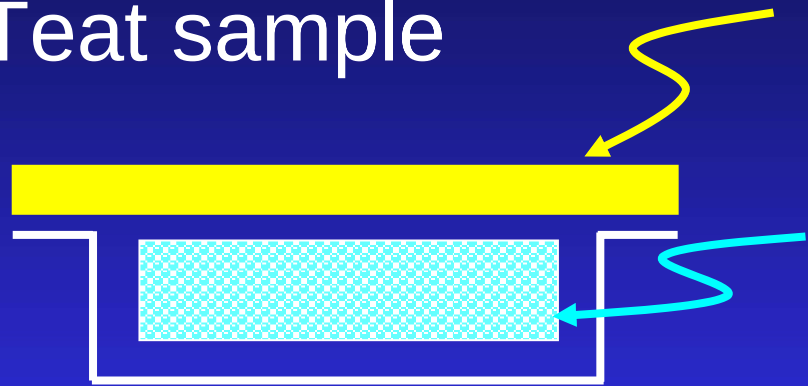
(1) OTR: 20^{o}C-85%RH/100%RH

OTR after Gelbo Flex



Reliability of Gas Barrier
- Lidding film -

Teat sample



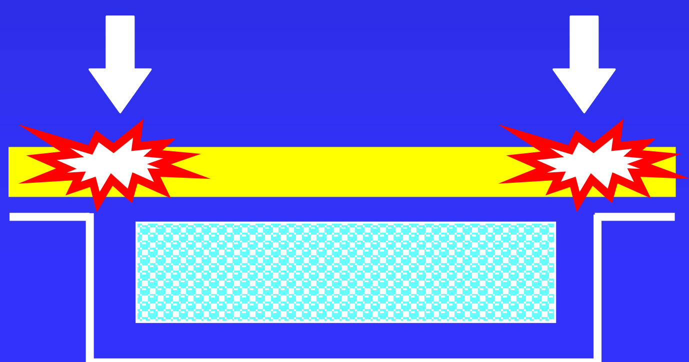
Lidding film

Barrier film//PA film//CPP film

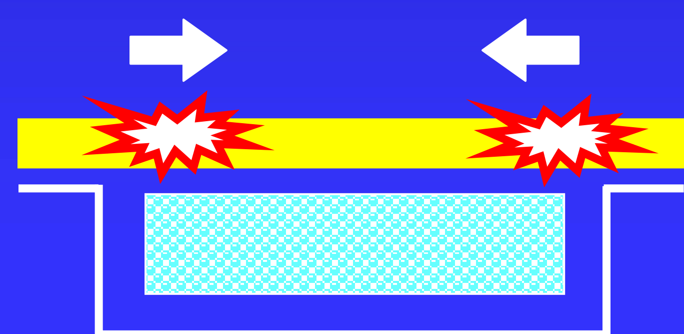
Gel

Gel + O_2 → Blue gel

Damage by heat seal

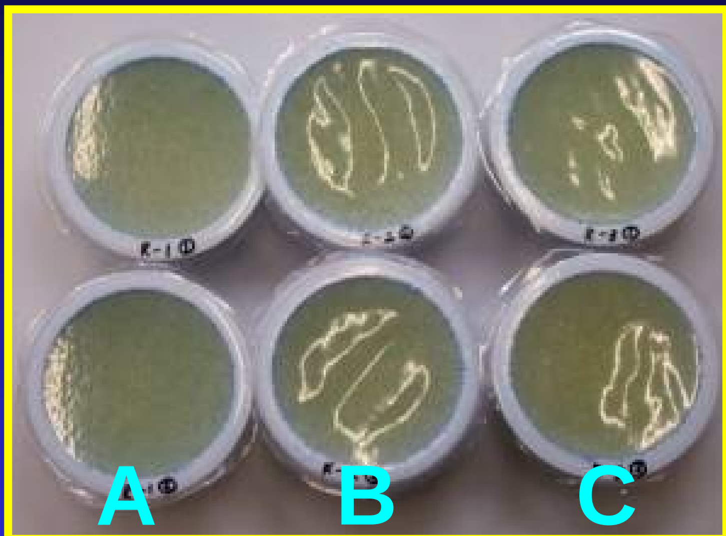


Damage by shrinkage

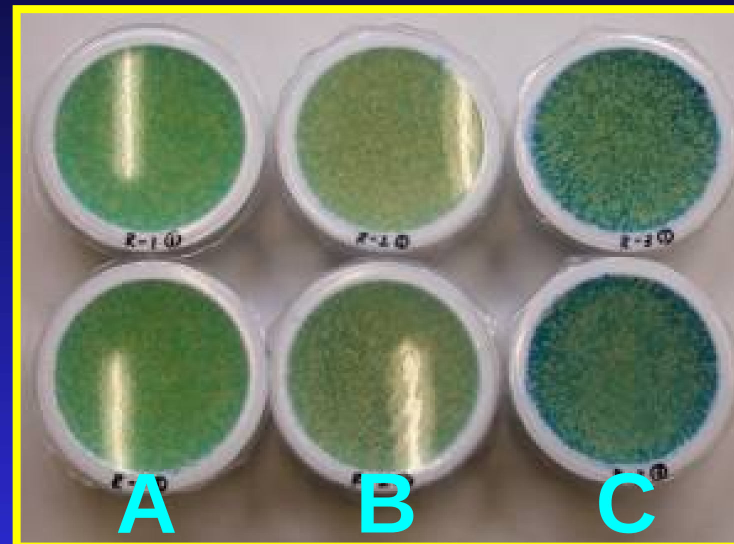


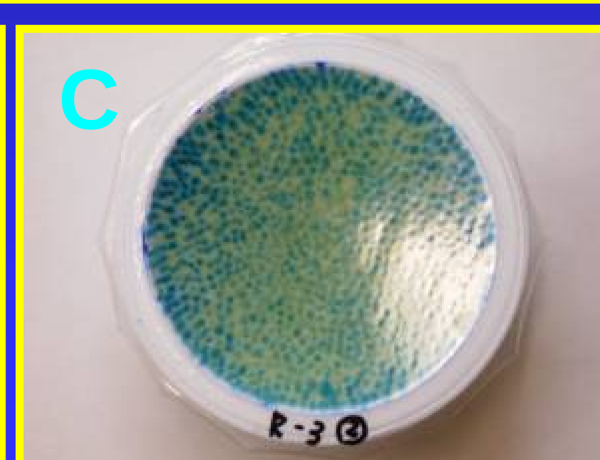
Lidding Film

Before retort



After retort





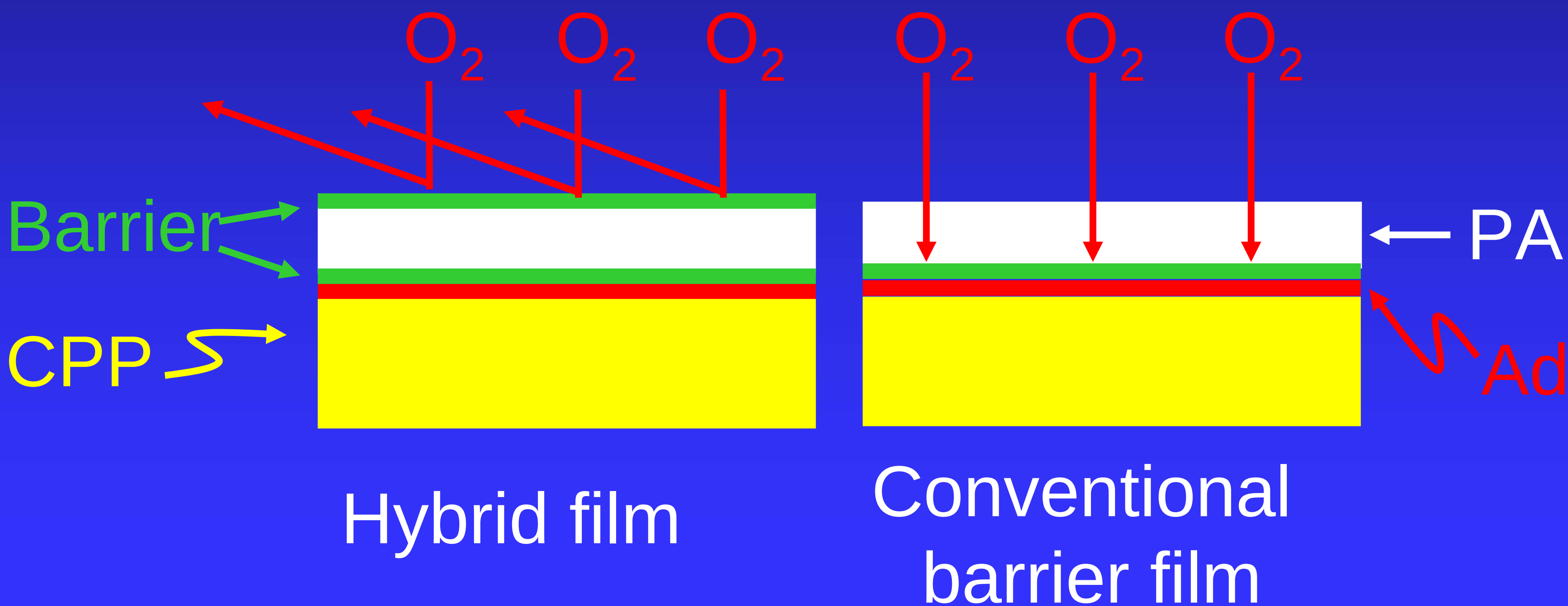
EVOH film

PET based
Hybrid film

PET based
Inorganic coated film

Deterioration of PA During Retort

- Deterioration by oxygen attacks during retort
- Protection by hybrid gas barrier layer



Mechanical Properties of Laminated Film

Measurement items		Units	PA based hybrid film//CPP film		PA film//CPP	
			Before retort	After retort	Before retort	After retort
Tensile strength at break	MD	MPa	63	65	65	41
	TD		60	55	65	39
Elongation at break	MD	%	83	90	100	40
	TD		93	82	100	40
Tensile modulus	MD	GPa	1.3	1.1	0.99	0.80
	TD		1.2	1.0	0.96	0.65
Puncture resistance		N	8.5	8.6	10.0	6.9
Impact strength		J	0.98	1.1	1.2	0.36

Conclusions

- Excellent and consistent gas barrier properties
- Gas barrier independent of retort conditions
- Gas barrier not affected by humidity, elongation, scratching nor flexing
- Easy printing without surface pre-treatment
- Easy handling: no curl, very low coefficient of friction

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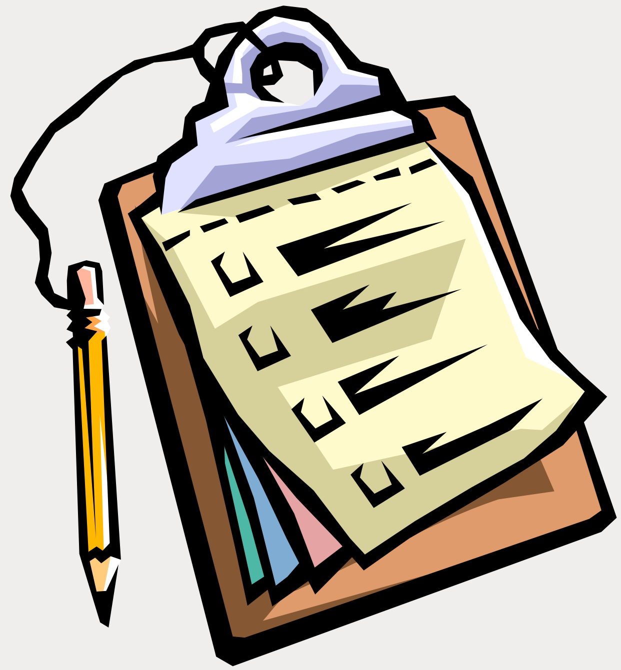

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