Ultra-Low Permeation Barrier Material for Global Fuel Line & Hose Designs

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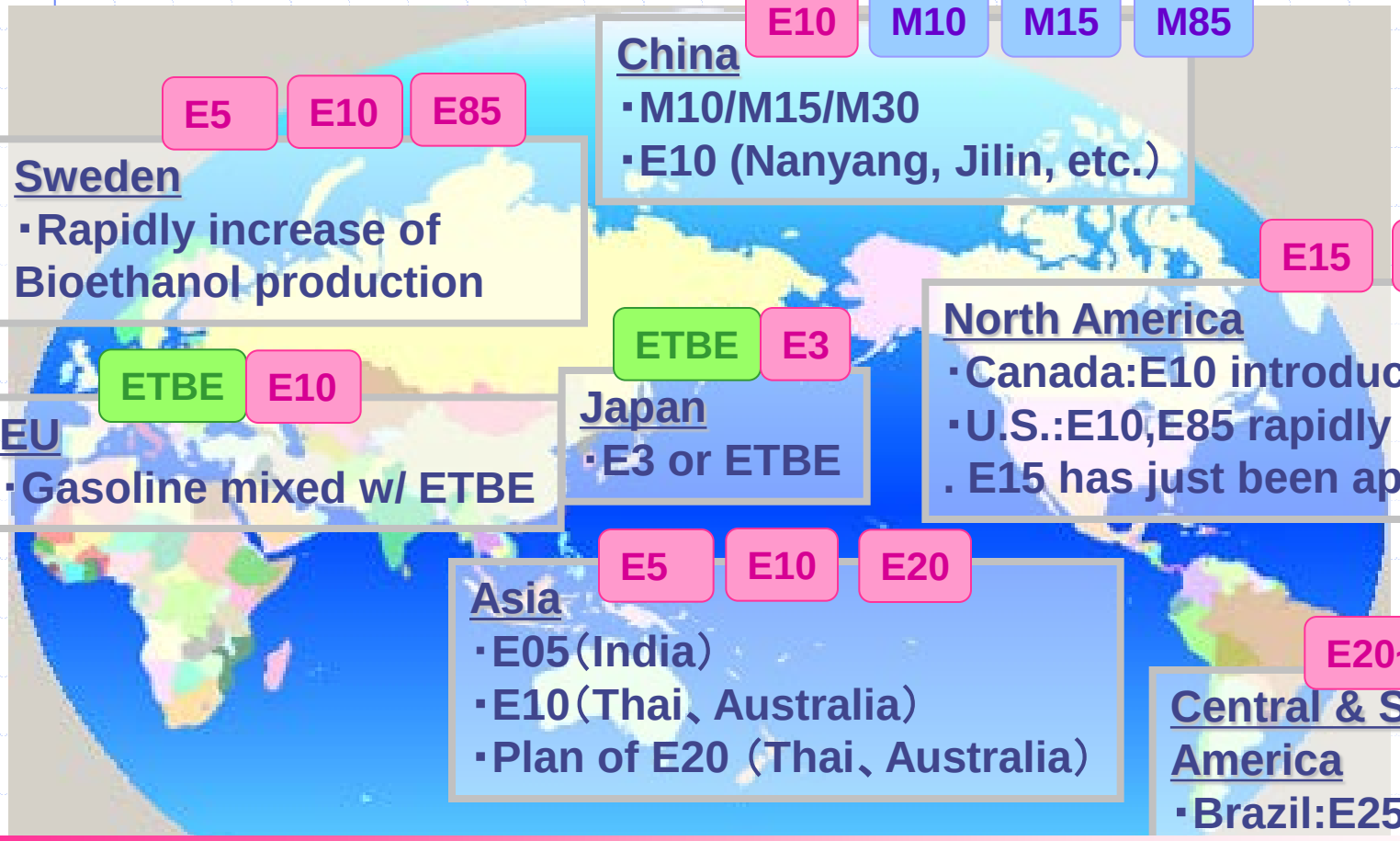
Alcohol mixed Gasoline worldwide



China
E10 M10 M15 M85
・M10/M15/M30
・E10 (Nanyang, Jilin, etc.)

Sweden
E5 E10 E85
・Rapidly increase of Bioethanol production

North America
E15 E85
・Canada:E10 introduction
・U.S.:E10,E85 rapidly increase
. E15 has just been approved

Japan
ETBE E3
・E3 or ETBE

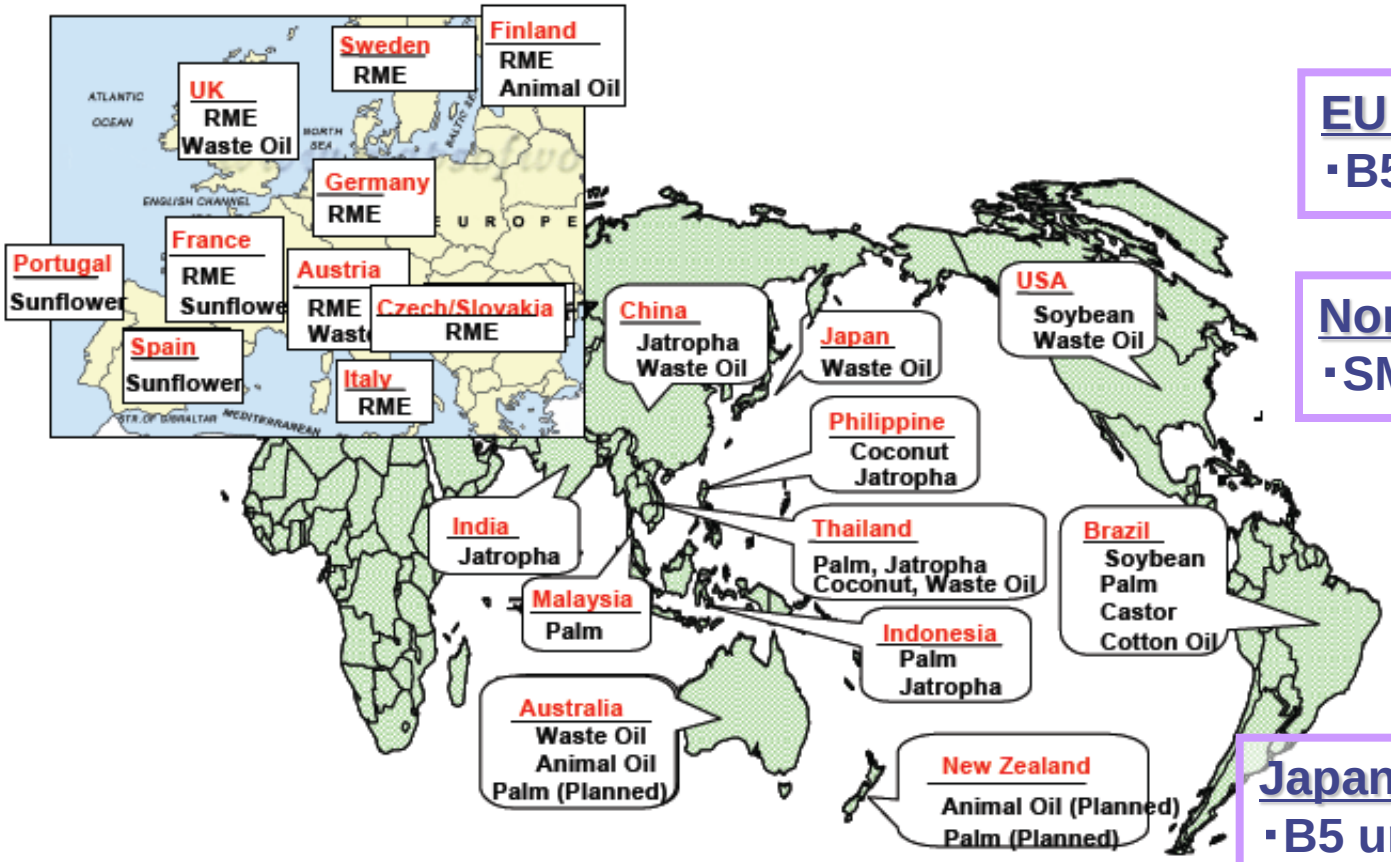
EU
ETBE E10
・Gasoline mixed w/ ETBE

Asia
E5 E10 E20
・E05（India）
・E10（Thai、Australia）
・Plan of E20（Thai、Australia）

Central & South America
E20~25 E100
・Brazil:E25 and E100

Evaporative Emission Regulations are becoming more stringent !!(including changing test fuel from gasoline to alcohol mixed fuel)

Bio-diesel fuel worldwide



EU B5 B30
- B5 is obligated, ~B100

North America B2 B20
- SME rapidly increase.

Asia B5 B10
- B5（India）
- B10（Thai）

Japan B5 B100
- B5 under consideration , Partially introduced B100.

Peroxide+High Temperature

(Continuous: 90~125 °C (Peak: 130~140 C))

very aggressive environments

Regulation and Flexible Fuel

Regulation (USA)

Emission			2004	2005	2006	2007-
USA	LEV2	0.5g/test	25%	50%	75%	100%
California	LEV2	0.5g/test	40%	80%	100%	100%
	PZEV	0.054g/test			10%	

LEV3 (2014 ???)
1.Test Fuel ⇒ E10
2.Permeation ⇒PZEV

Very stringent requirements

Flexible Fuel

Gasoline
NA and EU ・・・・E10, E85
China ・・・E10, M15, M30
South America ・・・E25,E100
Bio Diesel
SME, RME

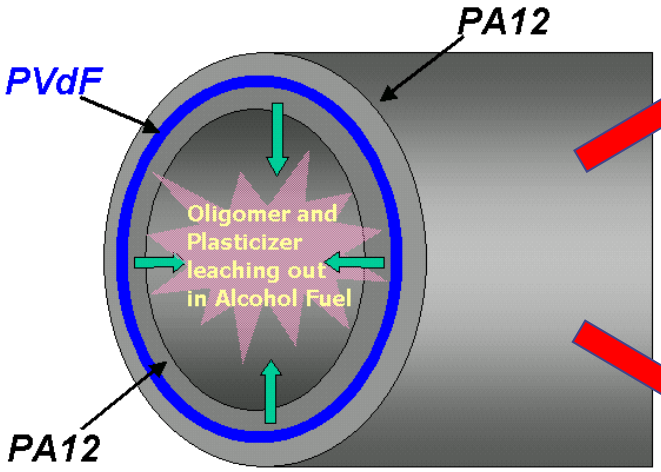
Both Fuel resistance and low permeation are important !

Current Trend

Trend is toward global fuel line standardization so that one or two constructions can provide excellent barrier toward all kinds of fuels.

Trend is to use fluoro-polymer as the fuel contact layer.

Fluoro-polymer as the fuel contact layer



The swell of inner material increases

Wash up problem

Extractable after fuel soaking

Conductivity loss problem (MΩ/sq)

		soaking time(hrs)				
Fuel	Inner layer	0	30	45	75	355
CE10	PA12 (4Layer)	0.01	no	no	no	no
	PA12 (2Layer)	0.04	no	no	no	no
	cond.EFEP(5Lyer)	0.09	0.21	0.23	0.25	0.22
	cond.EFEP(2Lyer)	0.02	0.02	0.02	0.02	0.02
	cond.CPT(2Layer)	0.02	0.02	0.02	0.02	0.02
CE85	PA12 (4Layer)	0.01	no	no	no	no
	PA12 (2Layer)	0.04	no	no	no	no
	cond.EFEP(5Lyer)	0.08	0.10	0.09	0.10	0.09
	cond.EFEP(2Lyer)	0.02	0.02	0.01	0.02	0.01
	cond.CPT(2Layer)	0.02	0.02	0.02	0.02	0.02

Drying time is one minute.

Fluoro-polymer is suitable for Inner layer material

Daikin Barrier Technology
-for managing such challenges-

EFEP:	Low permeation with excellent processibility
ETFE:	Very low permeation with increased temperature resistance
CPT(*):	Ultra-low permeation for PZEV applications

(*) New Development

Daikin Barrier Technology

Main Features :

		EFEP	ETFE	CPT
		RP-5000*	EP-7000*	LP-1000*
Temperature Resistance		4	4~5	4~5
Permeation Resistance		3	4	5
Flexibility		3	3	4
Processibility		5	4	3
Conductive Grade		Yes	No**	Yes
Bonding	Polyamide	Yes	Yes	Yes
	EVOH	Yes	No	No
	Rubber	No	No	Yes

Rating: 1=Lowest and 5=Highest

* Reactive grades. ** AS grade based on non-reactive ETFE is available.

Permeation and Modulus of Polymers for Fuel Line application

				Daikin Materials for Fuel Application			Reference					
				EFEP	ETFE	CPT	THV		PPA	PA9T	PPS	EVOH
				RP5000	**EP7000**	**LP1000**	A	B	**C**	**D**	E	F
Flex Modulus			MPa	1000	815	610	525	410	1500	※ 1350	※ 1300	※ 3500
Permeation	CE10	**60℃**	g*mm /m2/day	6.5	2.5	**0.4**	2.5	10	1.1	1.0	2.8	0.3
		40℃		0.60		**0.05**				0.38	0.60	0.08
	CE85	**60℃**		0.9	0.7	**0.2**						4.5
	CM15	**60℃**		11.5	5.5	**0.8**					8.4	35

※Tensile Modulus

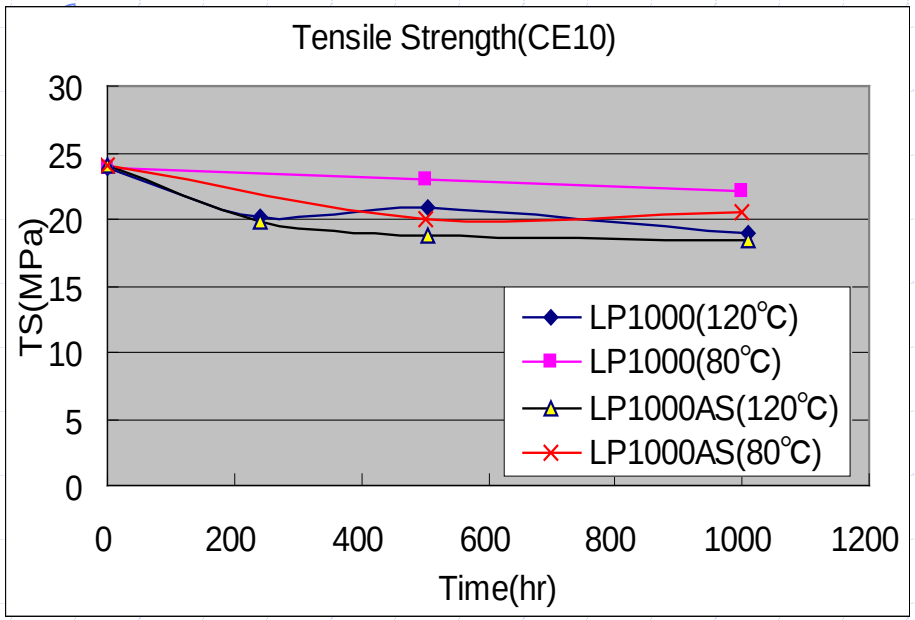
CPT has both ultra low permeation and low modulus !!!

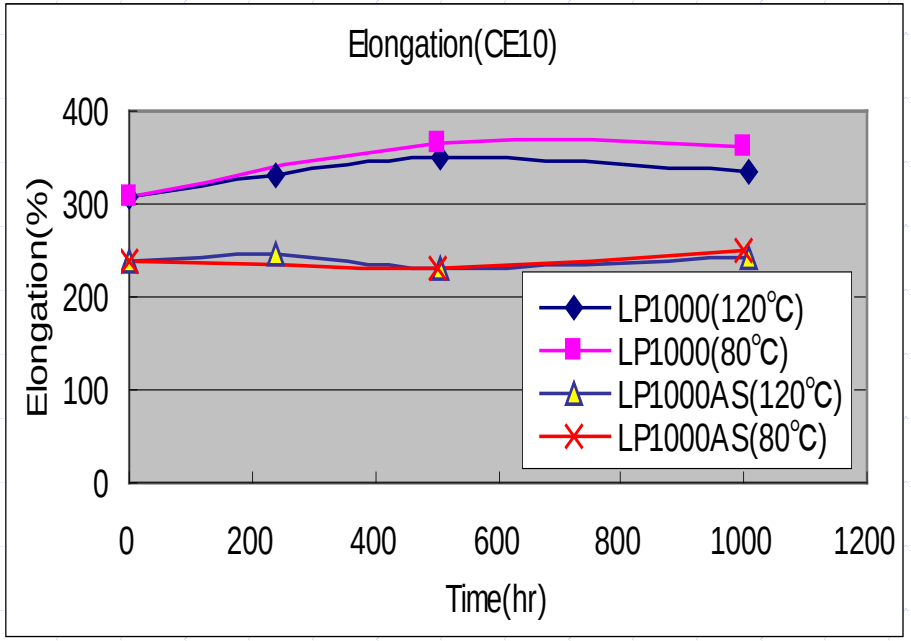
Daikin Barrier Technology

Basic Properties:

	RP-5000	RP-5000AS	EP-7000	LP-1000	LP-1000AS
Melting Point [C]	195	195	255	240	240
Static dissipation	No	Yes	No	No	Yes
Temperature of Impact Brittleness [C]	N/A	N/A	N/A	N/A	N/A
Density	1.74	1.76	1.76	2.1	2.1
Tensile Strength [MPa]	36~56	29~50	30~50	23~28	24
Tensile Elongation [%]	360~520	200~350	365~525	280~330	235
Tensile Modulus [MPa]	800	> 1000	800	500	750
Hardness ShoreD	60~70	-	75	56	N/A
Hardness ShoreA	N/A	N/A	N/A	N/A	N/A
MFR (49N) [g/10 min]	20~30 (265 C)	2~8 (265 C)	15~25 (297 C)	24~34 (297 C)	4~9 (297 C)

Alcohol Fuel Compatibility Test





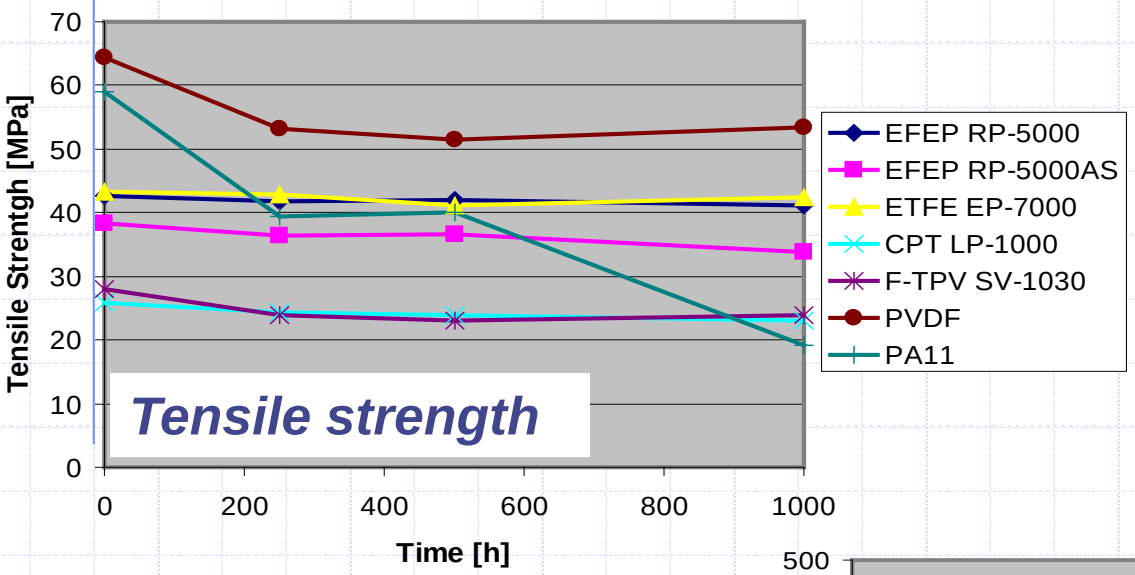
Bio-diesel Compatibility Test

Test procedure:

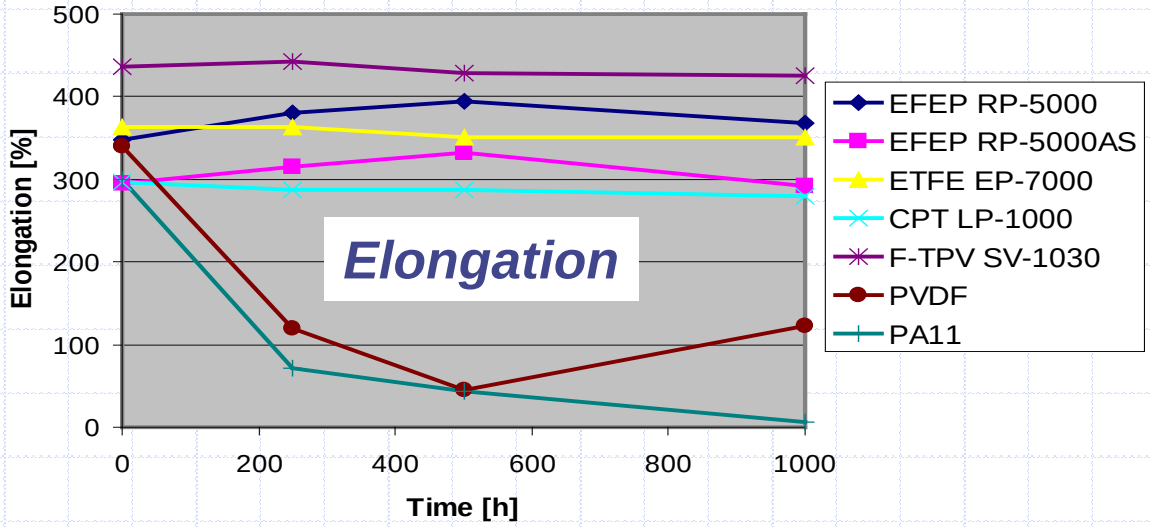
- Immersion of dumbbells in B100 (SME based)
- B100 maintained at 125 ^{o}C, fuel change every 250 hrs
- High peroxide test: Pre-heating + air bubbling of B100 to create high peroxide numbers (PN)

Time (h)	0	250	250	500	500	750	750	1000
PN	1880	121	1382	28	2251	21	2332	13

Biodiesel Compatibility



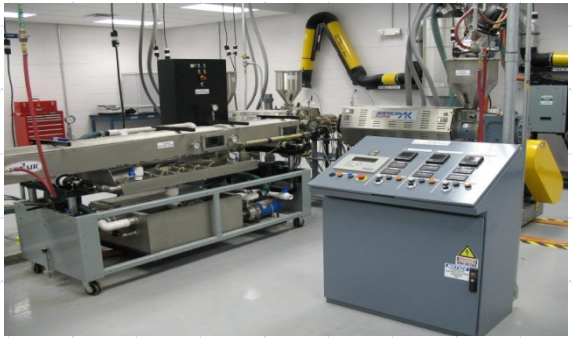
after Heat Ageing
in B100 (SME)
at 125 °C



Properties of PA12/Conductive CPT Tube

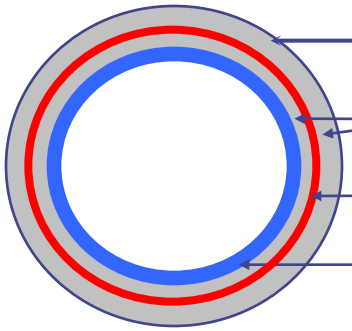
			New system		Current system	
			Low plasticizer	**High plasticizer**	Low plasticizer	High plasticizer
			PA12/CPT LP1000AS	**PA12/CPT LP1000AS**	PA12/RP5000AS	PA12/RP5000AS
Thickness		mm/mm	**0.8/0.2**	**0.8/0.2**	0.75/0.25	0.75/0.25
TS	SAE J2260	MPa	**40**	**33**	41	36
EL		%	**210**	**225**	248	235
Modulus		MPa	**750**	**440**	790	500
Cold Impact		failure/test	**0/5**	**0/5**	0/10	0/10
Burst Pressure		MPa	**9.3**	**6.8**	8.5	6.6
Surface Resistance		Mohm/sq	**0.07**	**0.06**	0.10	0.08
	2400 hrs	Mohm/sq	**-**	**0.05**	-	-
Permeation	CE10,60C	g/m2/day	**-**	**1.6**	19	15
Adhesion Strength after soaking	initial	N/cm	**can not peel**	**can not peel**	can not peel	can not peel
	2400 hrs		**-**	**can not peel**	can not peel	can not peel

Low Plasticizer PA12 : Evonik Vestamid LX9011
High Plasticizer PA12: Evonik Vestamid X7297



Near Zero Permeation Technology

Combination of CPT and EVOH achieves near zero permeation!!



Polyamide
Tie (PA)

Permeation Condition CE10, 60 °C

t:0.8mm P: 100-300g*mm/day/m^2

EVOH t:0.1mm P:0.3g*mm/day/m^2

Neoflon CPT t:0.1mm P:0.4g*mm/day/m^2

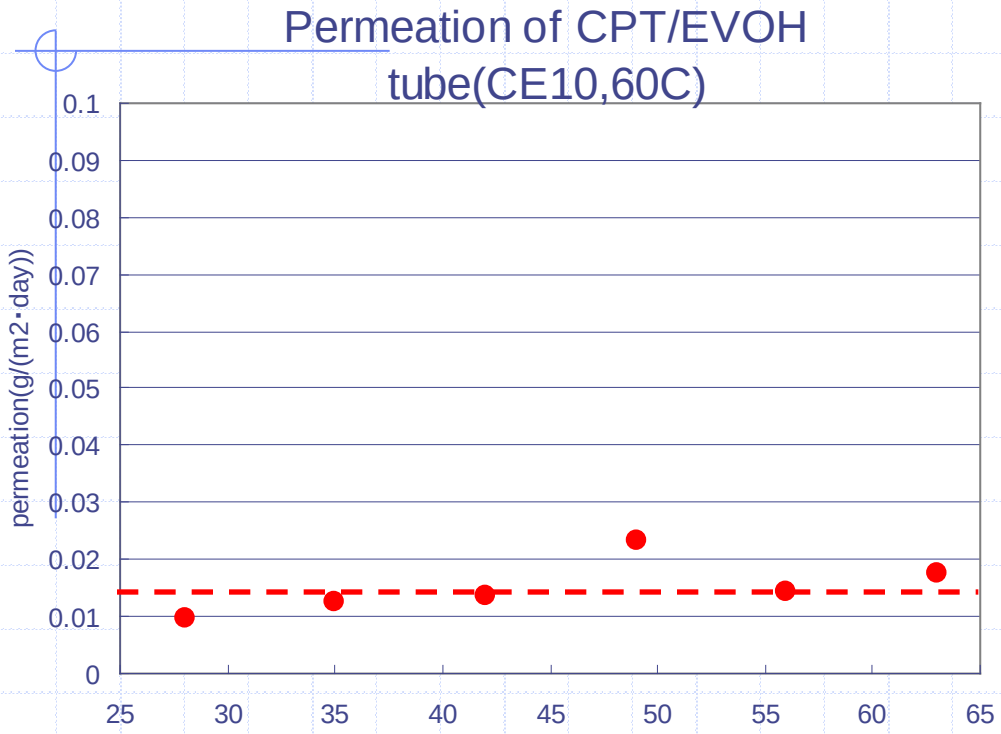
Calculation of MLT-Permeation

$$T_{tube}/P_{tube} = \Sigma\, t_i / P_i$$

$$1/P = \underbrace{0.1/0.3}_{\text{EVOH}} + \underbrace{0.1/0.4}_{\text{CPT}} + \underbrace{0.8/100\sim300}_{\text{Polyamide,HDPE}}$$

$P=1.7(g/day/m^2)$ **similar to that from CPT/PA12 two layer tubing but…**

Near Zero Permeation Technology



Actual permeation rate is

0.01 – 0.03 g/day/m^2 (average)

≒1/100 against calculation

≒1/1000

vs. current EFEP solution

What causes this synergism ?

Fuel barrier of EVOH (g-mm/m^2 - day)

Polymer	Fuel C	CE20
EVOH (32 mole% Et)	6x10^{-5}	1.32

Fuel vapor barrier of EVOH is very dependent on the amount of alcohol present in the fuel. When EVOH is buried inside the multilayer structure, the equilibrium alcohol content at the EVOH layer boundary can be very low. Effectively EVOH's fuel barrier performance may approach that of fuel C in a sandwiched construction.

New Concept of Low Permeation Multi-Layer Rubber Hose (Using CPT as Barrier)

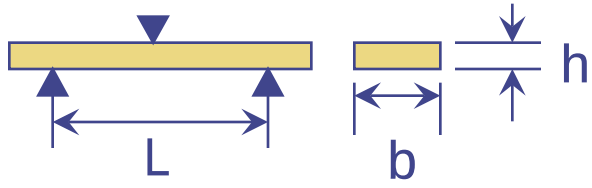
When CPT can be bonded with Rubber:

Since CPT has ultra low permeation and very low modulus, it offers a great deal of flexibility in multilayer hose design by controlling thickness of CPT layer.

Ex: When the thickness of CPT is reduced to half.

1. Permeation is inversely proportional to thickness
   - ➡ Permeation become double ➡ still very low permeation

2. Load(=flexibility) is proportional to the 3rd power of thickness
   - ➡ Load becomes 1/8 ➡ More flexible than other materials for bonding to rubber



$E = L^3/(4bh^3) * F/Y$ Y : Strain

3. Barrier material cost is in direct proportion to thickness
   - ➡ Barrier material cost may be reduced

CPT Bonding Test Results with NBR

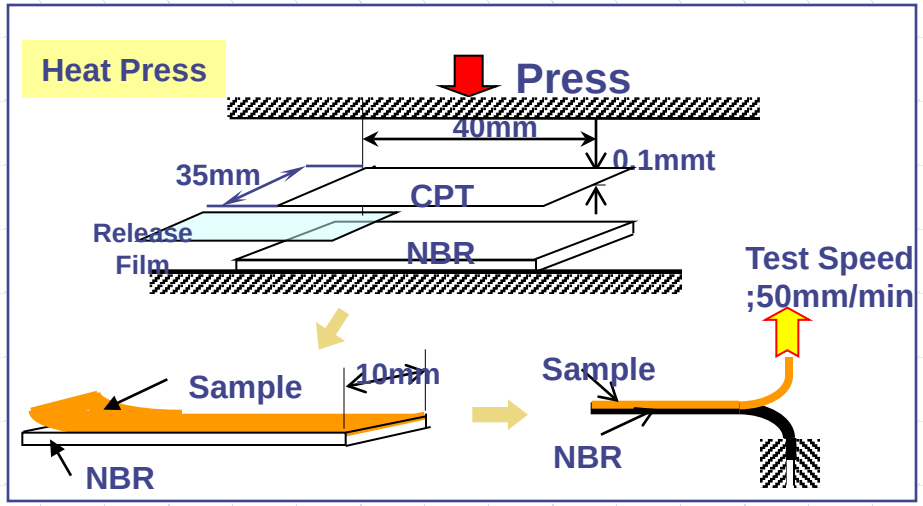
Heat Press Test Results

	Sample 1	Sample 2
Fluoro-polymer	CPT	CPT
NBR	NBR1 (Daikin recipe)	NBR2 (Daikin recipe)
Adhesion Strength（N/cm） 160 ℃ curing for 45 min	>20 Material Break	>20 Material Break

※The difference between NBR1 and NBR2 is the grade of adhesion promoters used.

Properties of NBR compounding (Daikin Recipe)

Hardness：Shore A 65～70
TS：16～17MPa
EL：500～600%

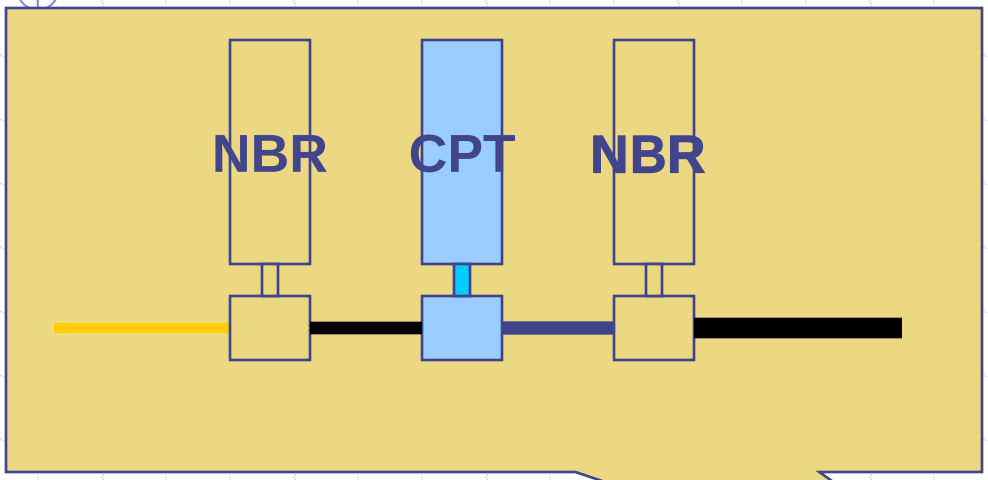


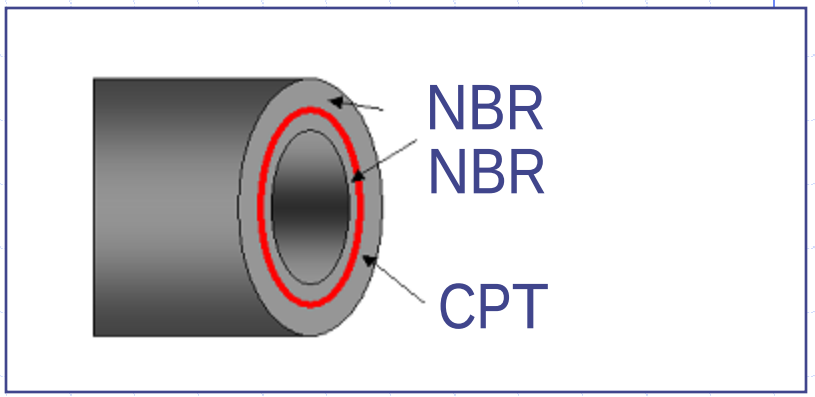
CPT Bonding Test Results with NBR

Adhesion Strength after soaking in CE10 at 60℃

soaking time	adhesion strength
0hrs	21- 24N/cm CPT material break
24hrs	N=1 17 N/cm CPT material break N=2 21 N/cm CPT material break N=3 18 N/cm CPT material break
96hrs	N=1 22 N/cm CPT material break N=2 20 N/cm CPT material break N=3 18 N/cm CPT material break
168hrs	N=1 18 N/cm CPT material break N=2 19 N/cm NBR material break N=3 18 N/cm CPT material break

CPT/Rubber Hose Molding Conditions





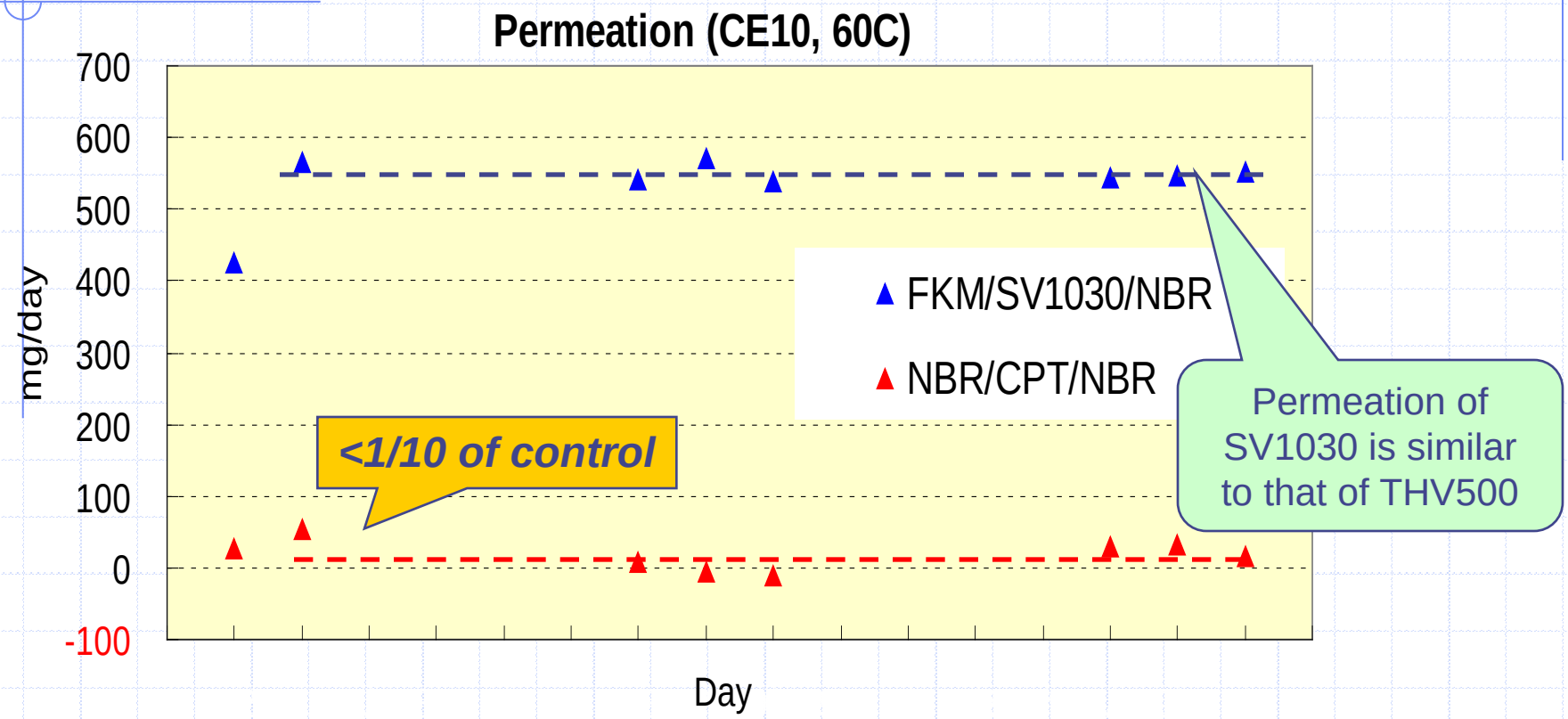
CPT Cylinder Temp:255-260 ℃

CPT Die Temp:270 ℃

NBR Cylinder Temp:70-80℃

NBR Die Temp:90℃

Permeation of Multi-Layer Hose



Conditions:

Length of hose: 250mm ID:24.8mm Insert length: 45mm

Inside area of hose:124 cm^2

Thickness of each layer: rubber/fluoro-polymer/rubber=2.4/0.2/2.4 (mm)

Filler Neck Hose (FRS)

Cond.NBR/CPT/NBR/Reinforcement/CPE

Sample shown here was made by Fluid Routing Solutions, Inc.

Summary

1) A new class of fluoropolymer, CPT, has been developed. It is characterized by a number of unparalleled properties such as excellent fuel barrier, very good alcohol resistance and biodiesel compatibility, good flexibility, great chemical resistance, and strong adhesion to various grades of polyamides or NBR.
2) By incorporating a thin layer of CPT into multilayer fuel tubes or hoses, fuel system designers can tailor their applications not only for more restrictive emission regulations, but also for more aggressive fuels (bio-diesel, alcohol blended fuels, etc.) at higher underhood temperatures.
3) Both natural and anti-static grades of CPT are available.

Thank you

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