Database of Polymeric Materials for Hydrogen Gas Seals and Dispensing Hoses

11 September 2018

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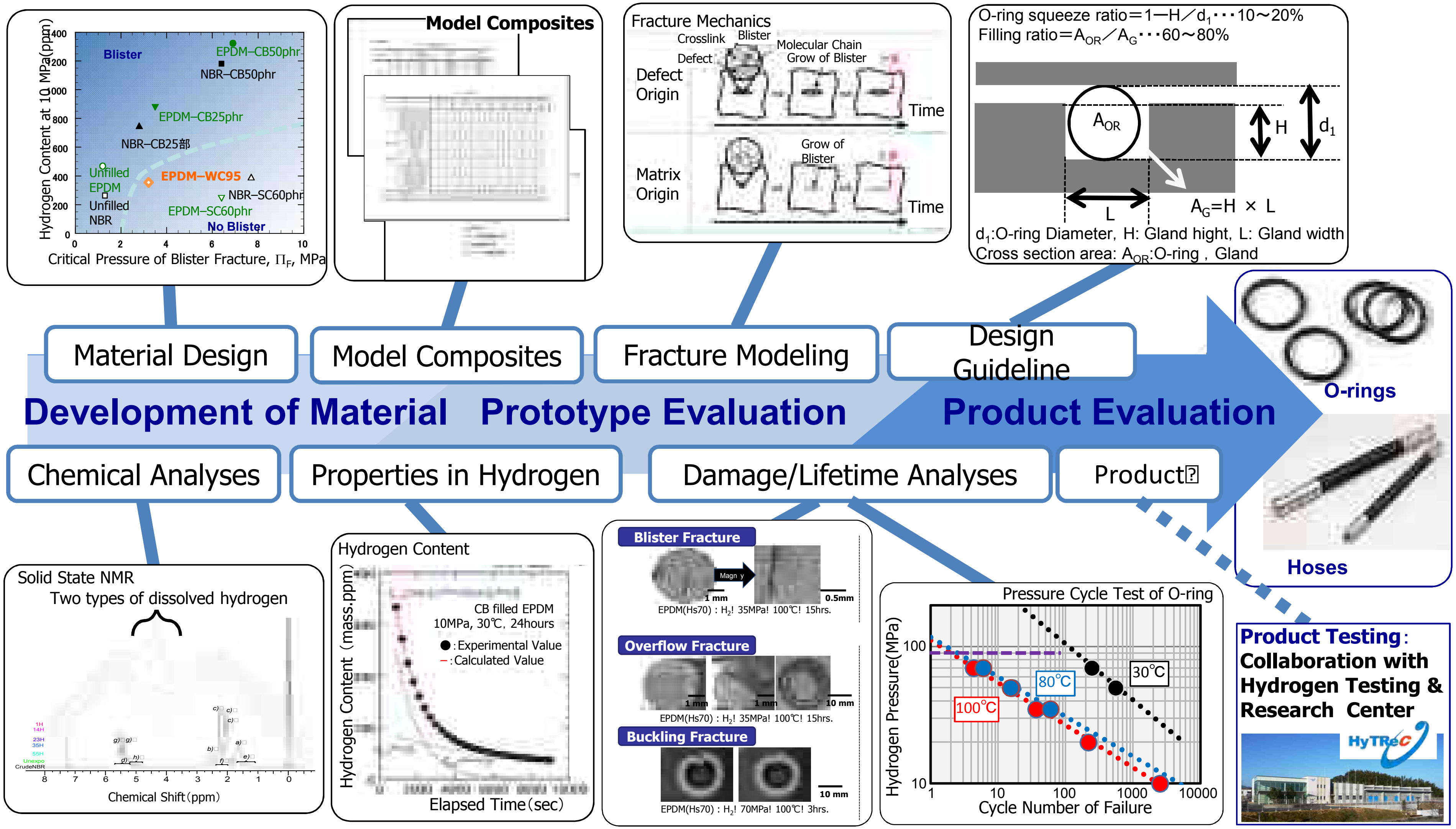
Acknowledgement
This research has been supported by the New Energy and Industrial Technology Development Organization (NEDO) "Hydrogen utilization technology development (2013–2017)".

Hydrogen Polymers in HYDROGENIUS

Rubbers materials and polymeric materials are **"KEY MATERIALS"** for hydrogen gas seal in equipment for hydrogen energy system.



Establishment of Research Group

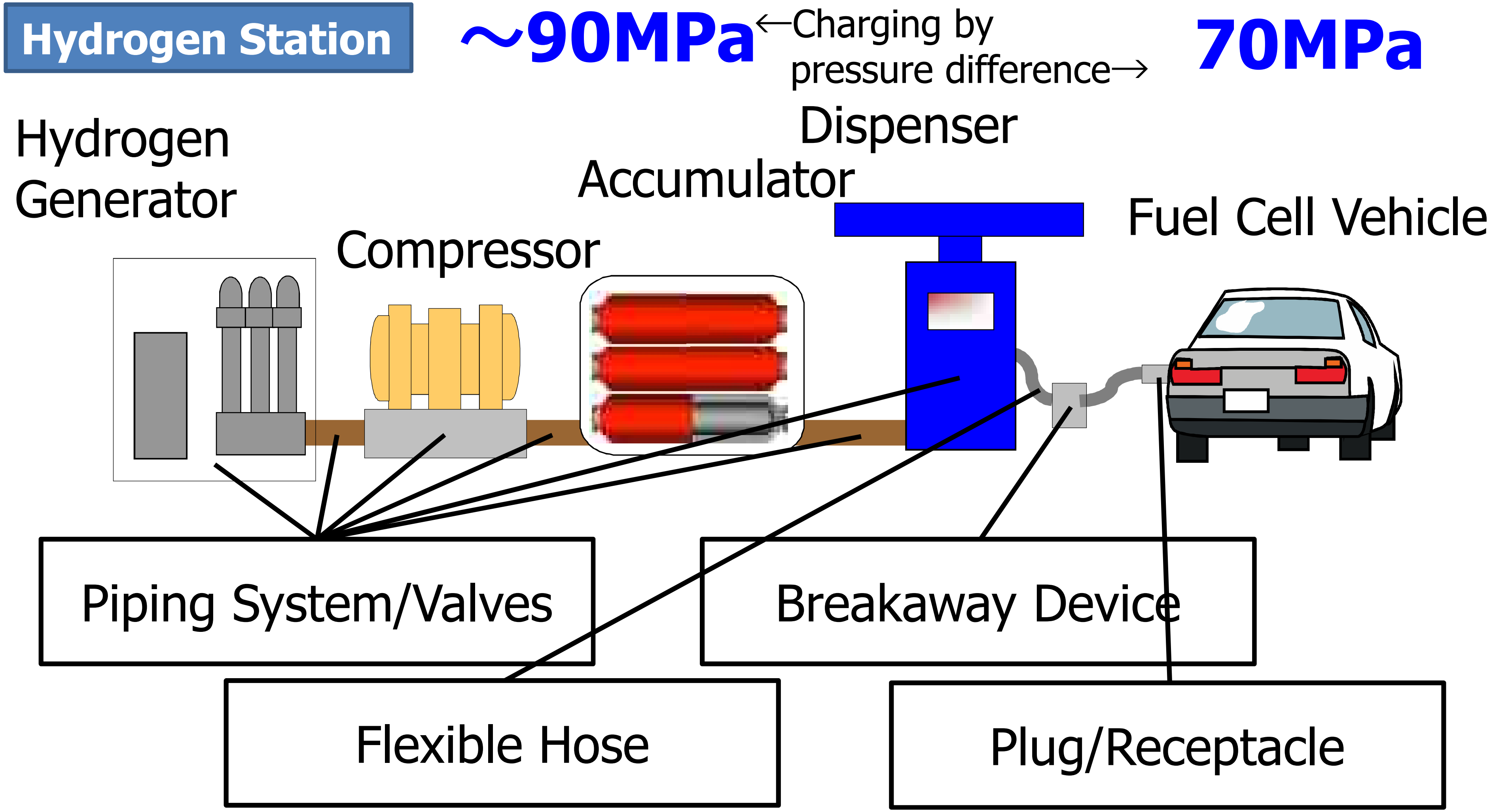
It is important to understand the relationship between structure of elastomeric compounds and their properties under high-pressure hydrogen.

We need diverse ideas from industries for the model compounds and hydrogen properties for measurement.

In 2012, we have established **"The Research Group of Elastomers for Hydrogen Equipment" in The Society of Rubber Science and Technology, Japan**.

In the research group, more than 40 members are active from the viewpoints of materials and elastomeric compounds design, hydrogen equipment design.

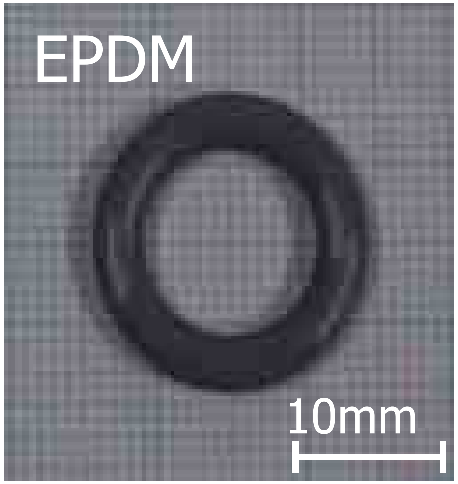
Polymeric Materials for Hydrogen Equipment



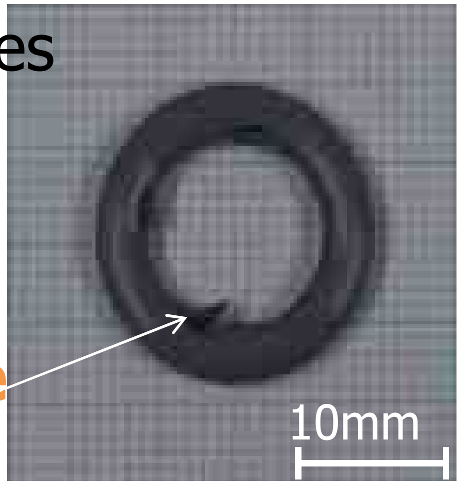
Rubbers and polymeric materials are used for gas seals and liners in the hydrogen equipment.

Fracture of O-ring by Hydrogen

Before test



90MPa,100°C ×20 cycles

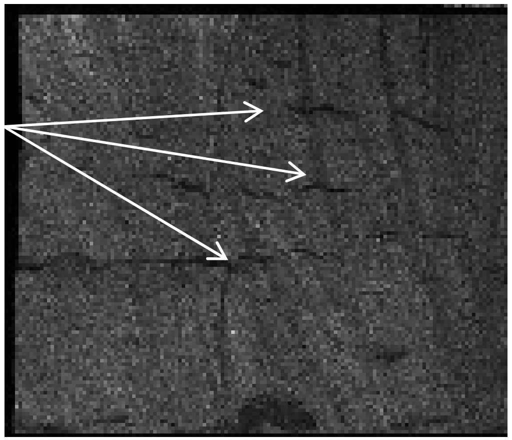


Fracture

after 100MPa, 30° C ×25 cycles

Seal Break

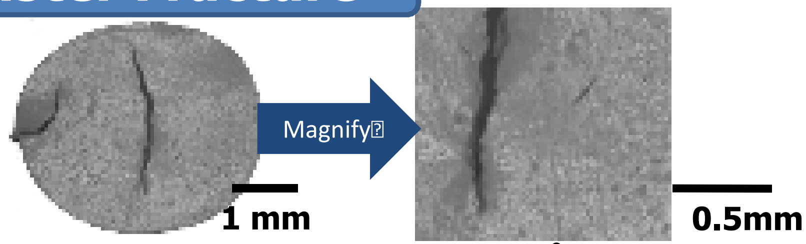
Cross section



Blister Fracture

Key Parameters for Fracture Modes of O-ring

Blister Fracture

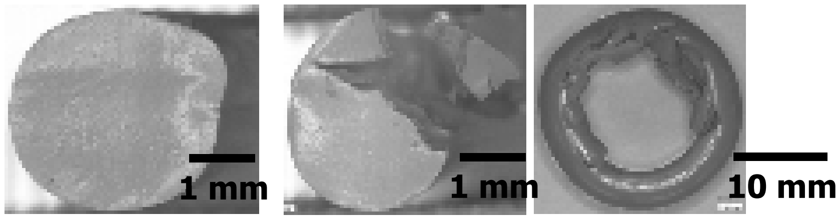


EPDM(Hs70) : H_2×35MPa×100℃×15hrs.

Material Strength and Hydrogen Solubility of Rubber Materials

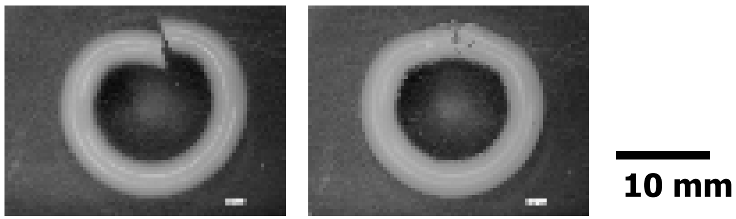
Key Parameter: H_2 content

Overflow Fracture



EPDM(Hs70) : H_2×35MPa×100℃×15hrs.

Buckling Fracture



EPDM(Hs70) : H_2×70MPa×100℃×3hrs.

Volume Increment of Rubber Materials originated from Swelling by Hydrogen

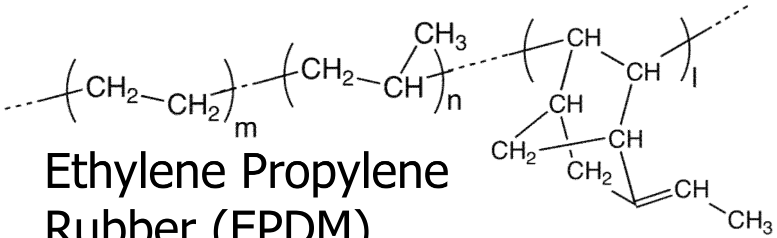
⇩

Gland Design in consideration for Volume Increment of the Rubber Materials

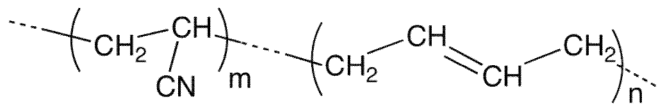
Key Parameter: Volume change

Design of Model Rubber Compounds

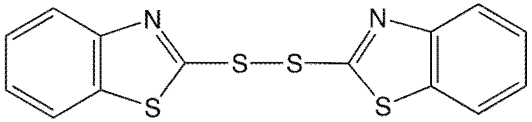
ITEMS	NBR NF	NBR CB50	NBR CB25	NBR SC60	NBR SC30	EPDM NF	EPDM CB50	EPDM CB25	EPDM SC60	EPDM SC30
NBR(Nipol 1042)	100	100	100	100	100	-	-	-	-	-
EPDM(Esprene 505)	-	-	-	-	-	100	100	100	100	100
Stearic Acid	1	1	1	1	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5	5	5	5	5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.7	0.7	0.7	0.7	0.7	0.5	0.5	0.5	0.5	0.5
ZnEDC	0.7	0.7	0.7	0.7	0.7	-	-	-	-	-
Carbonblack(N330)	-	50	25	-	-	-	50	25	-	-
Silica(Nipsil VN3)	-	-	-	60	30	-	-	-	60	30



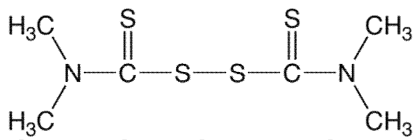
Ethylene Propylene Rubber (EPDM)



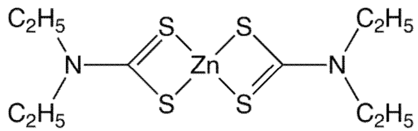
Acrylonitoril Butadiene Rubber (NBR)



2,2′-Benzothiazyl Disulfide (MBTS)



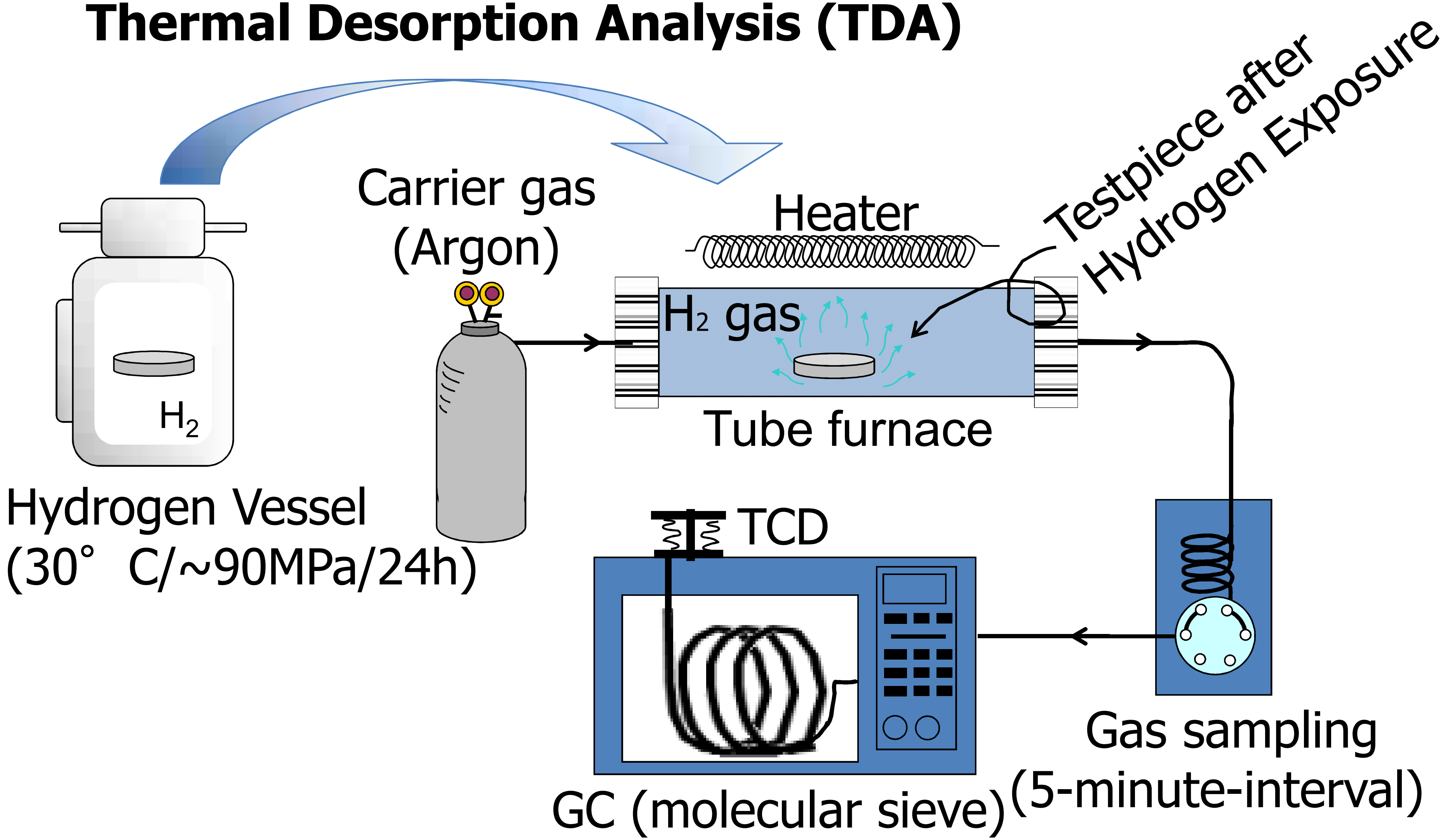
Bis(dimethylthiocarbamoyl) Disulfide (TMTD)



Zinc Diethylthio-carbamate (ZnEDC)

Measurement of Hydrogen Content

Thermal Desorption Analysis (TDA)

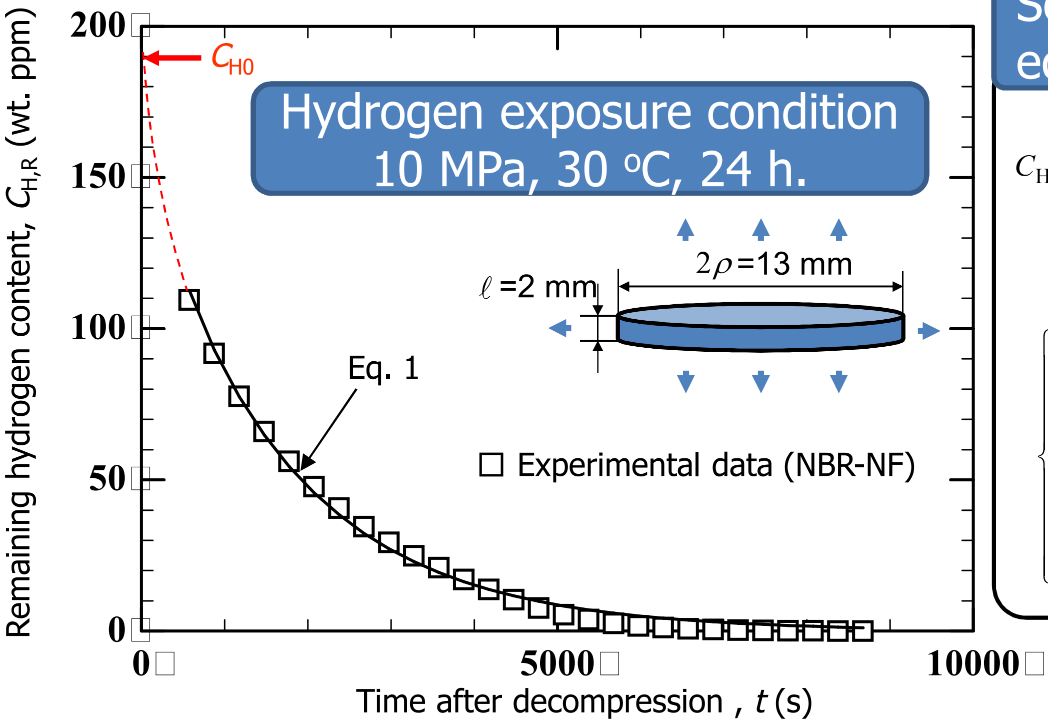


Hydrogen Exposure → Hydrogen content measurement (TDA)

Hydrogen Content Estimation

- After exposure to hydrogen gas, hydrogen content was measured by TDA.
- A large volume of hydrogen release is considered before the measurement tests.

⇒Eq. (1) was fitted to remaining hydrogen content by using the least square method regarding equilibrium hydrogen content and diffusivity as unknown parameters, and the equilibrium hydrogen content was estimated by extrapolation.



Hydrogen release profile of hydrogen–exposed specimen of NBR-NF.

Solution of unsteady diffusion equation at hydrogen release (5)

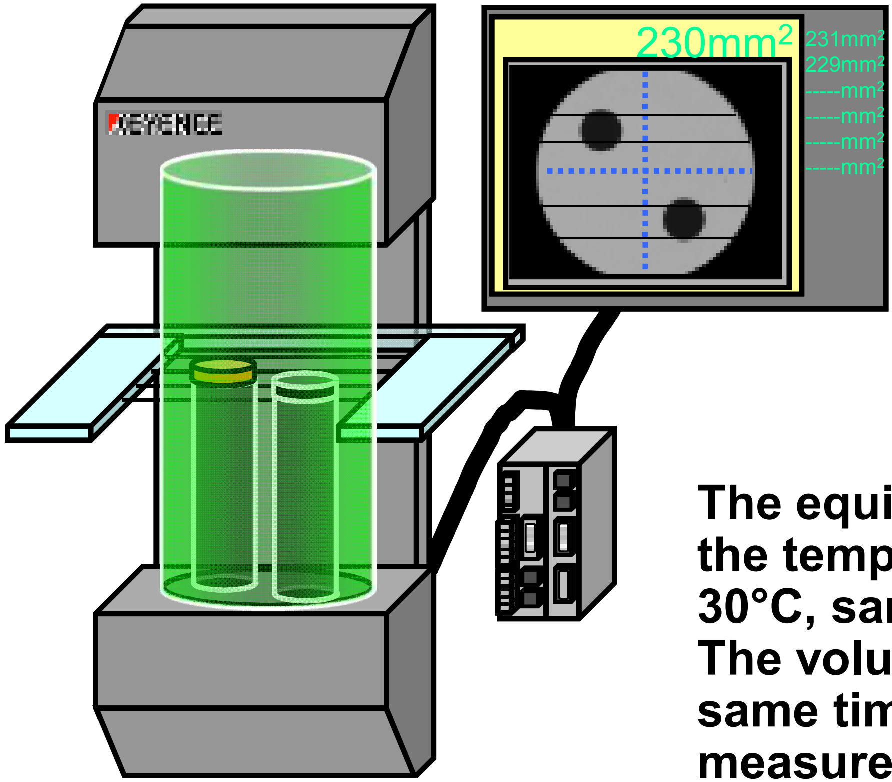
$$C_{H,R}(t) = \frac{32}{\pi^2} \times C_{H0} \times \left\{ \sum_{n=0}^{\infty} \frac{\exp[-(2n+1)^2 \pi^2 D t / \ell^2]}{(2n+1)^2} \right\} \times \left\{ \sum_{n=1}^{\infty} \frac{\exp[-D \beta_n^2 t / \rho^2]}{\beta_n^2} \right\} \quad \cdots \text{Eq. 1}$$

- $C_{H,R}(t)$: Remained hydrogen content at t (wt.ppm)
- C_{H0} : Equilibrium hydrogen content (wt.ppm)
- D : Diffusion coefficient (m^2/s)
- ρ : Radius of specimen (m)
- ℓ : Thickness of specimen (m)
- β_n : The root of the zero - order Bessel function

(5) A. Demarez, A. G. Hock, F. A. Meunier, Acta Metallurgica, 2, 214 (1954).

Volume Measurement System

KEYENCE 2D Silhouette Scanner TM-3000

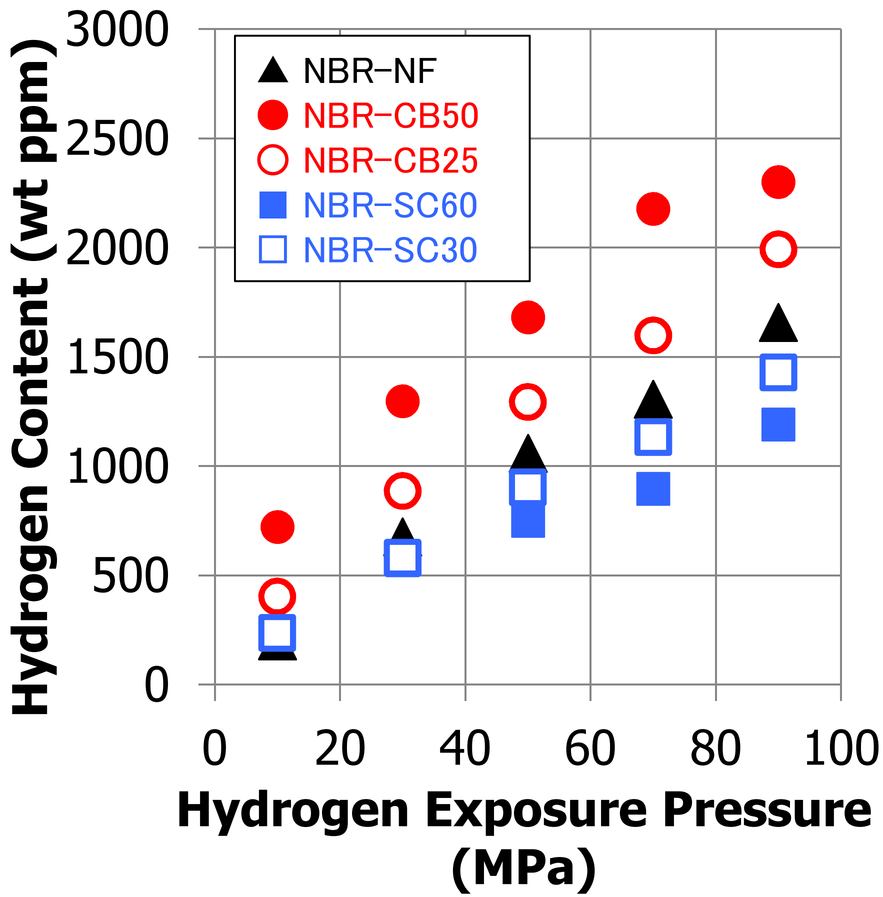


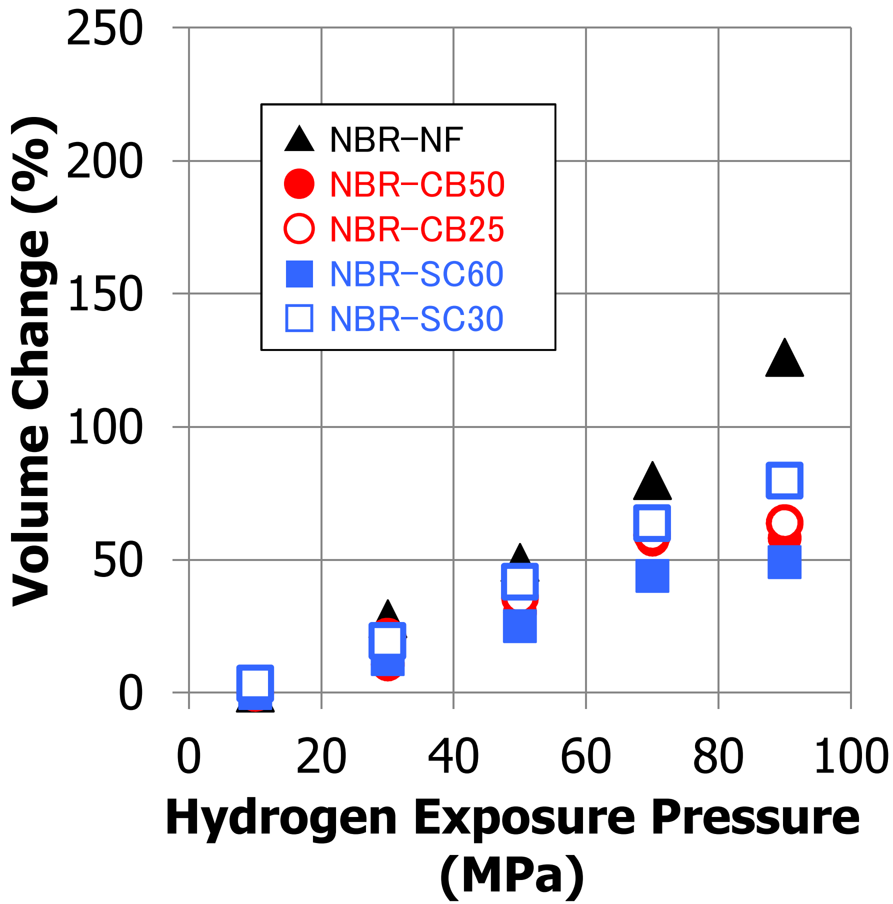
Measuremen Area	φ65mm
Detection Limit	0.5mm
Distance to Ditector	270mm
Light Source	InGaN LED
Dimensional	±3μm
Repeat Accuracy	±0.2μm
Measuremen	5.5ms
Sample Dimension	φ13mmx2mm

The equipment is in the thermostat chamber. the temperature of the chamber is controlled at 30°C, same as TDA measurement.
The volume of 8 samples can be measured at same time in every 5 minutes, same as TDA measurement.

The surface area of the sample (13mmφ×2mmt) can be measured .
The volume of the sample can be estimated by cube square root of the surface area.
The results are consistent with Archmedean method.

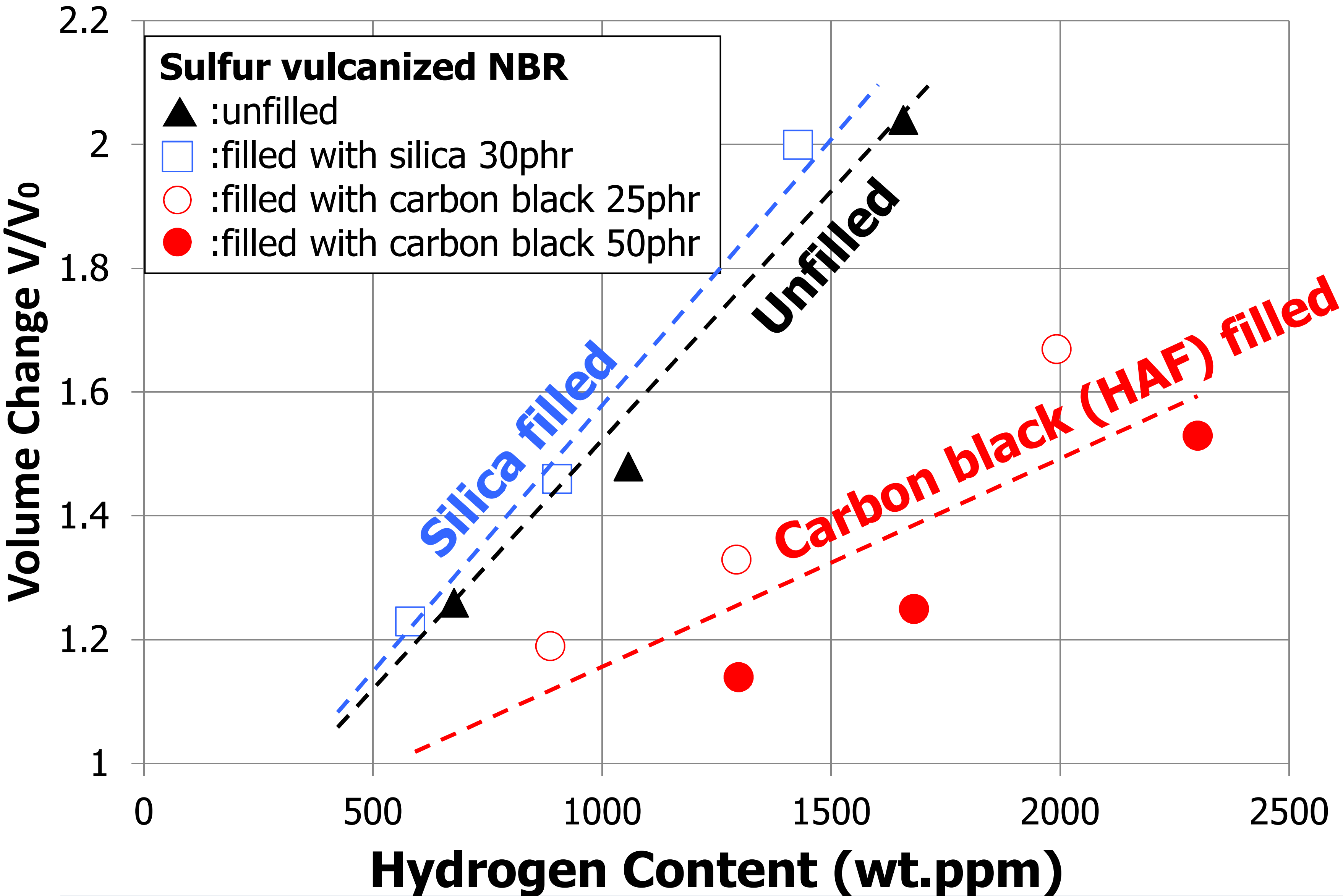
Exposure Pressure Dependency of Hydrogen Content





Hydrogen contents of model composites after hydrogen exposure are proportional to the hydrogen exposure pressure. Hydrogen contents of carbon black filled NBR are larger than those of unfilled and silica filled rubbers. Volume change of model composites after hydrogen exposure are proportional to the hydrogen exposure pressure. Filled rubbers shows smaller volume change.

Relationship between H_2 content and volume



Carbon Black controls volume change of the compound

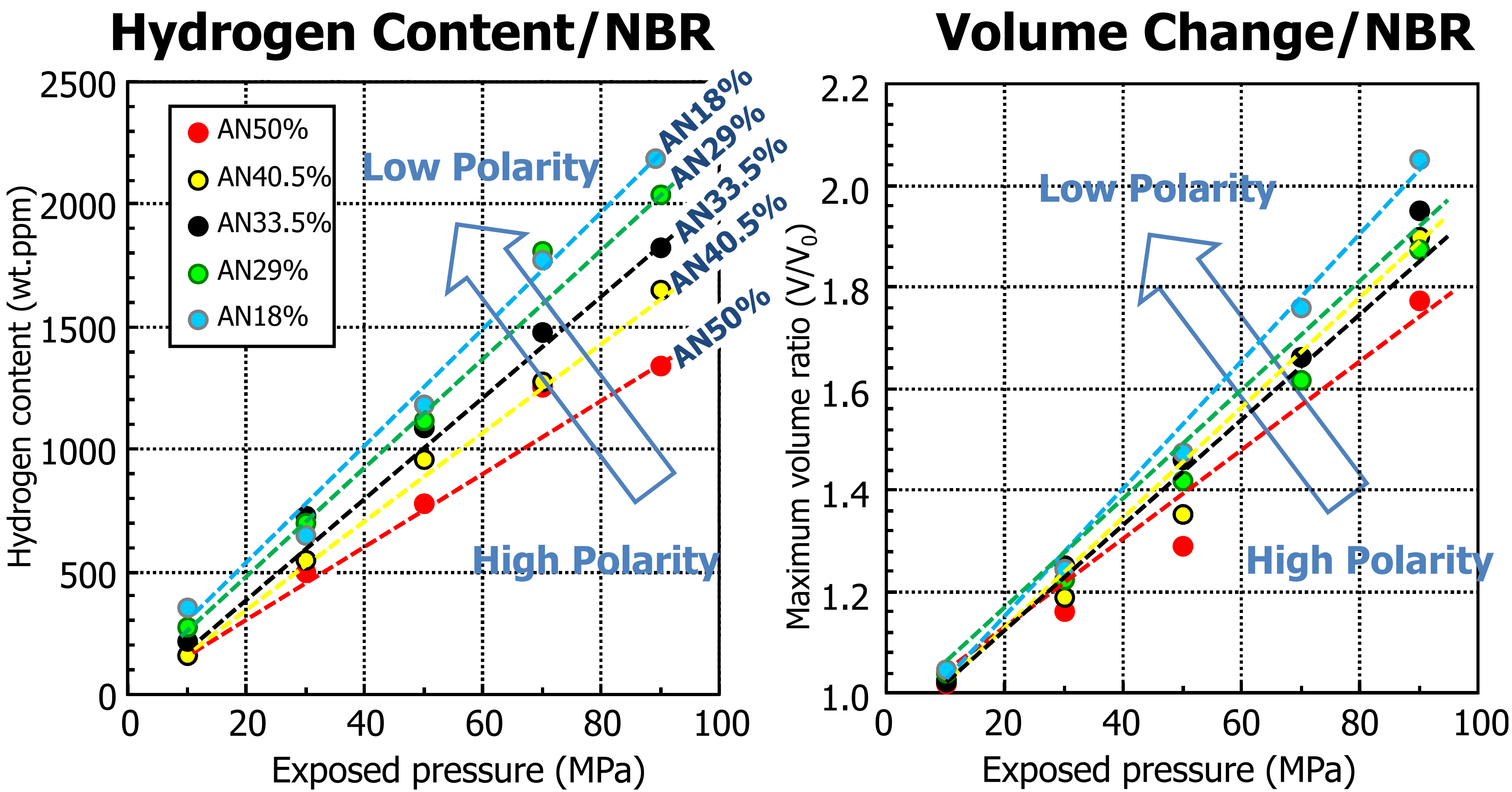
phr: weight parts per hundred weight parts of rubber

Model NBR Compound

Grade	Acrylonitrile Content	Density (g/cm^3)
Low Nitrile	18%	0.94
Mid Nitrile	29%	0.97
Mid-High Nitrile	33.5%	0.98
High Nitrile	40.5%	1.00
Very High Nitrile	50%	1.02

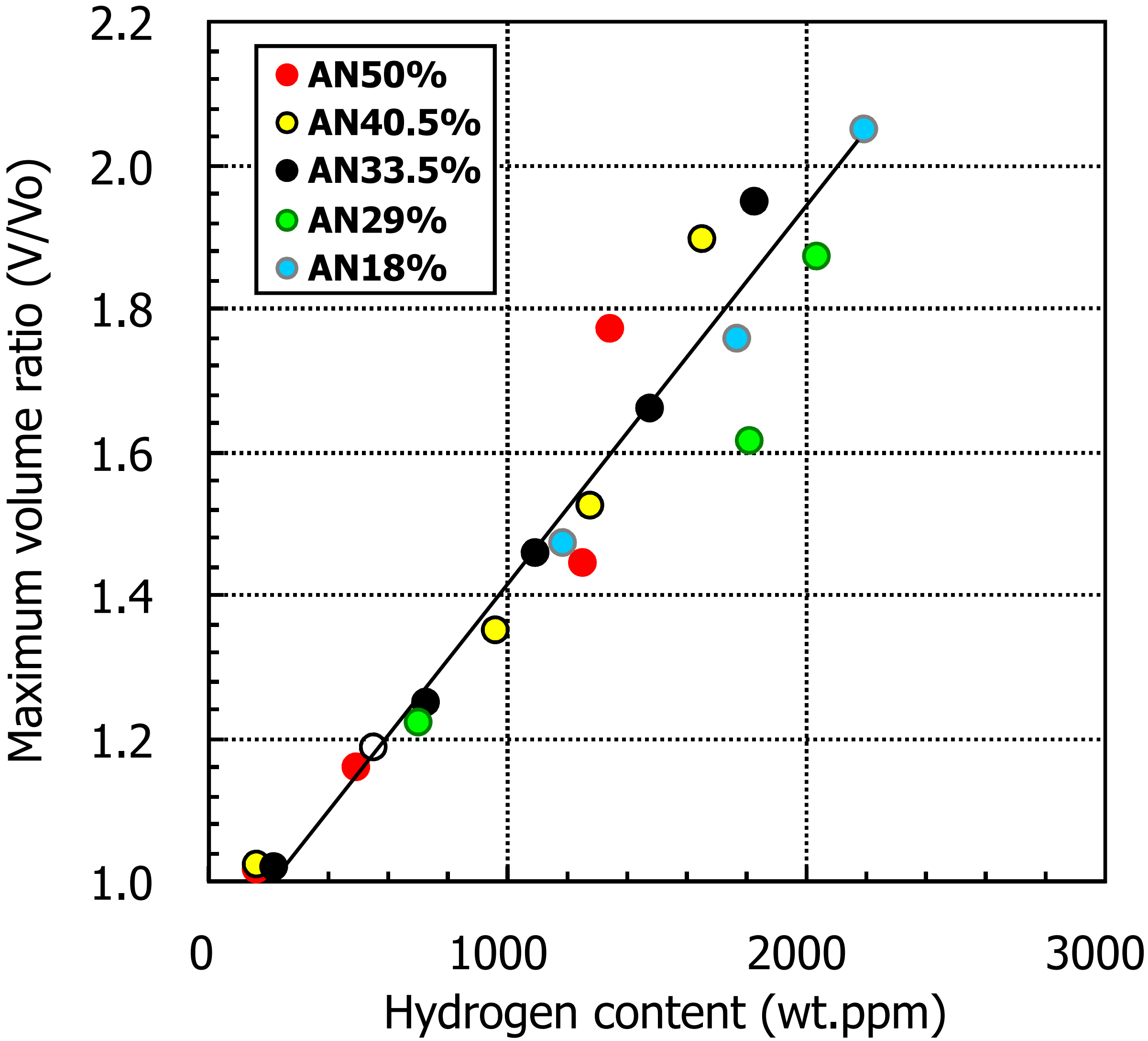
Compound:Sulfur vulcanization system
Sulfur:1.5 phr, MBTS:1.5 phr, TMTD:0.7 phr, ZnEDC:0.7 phr
Stearic acid: 1 phr, Zinc Oxide:5 phr

Unfilled NBR:Polymer Polarity



High polar NBR polymer suppress hydrogen penetration and volume inflation.

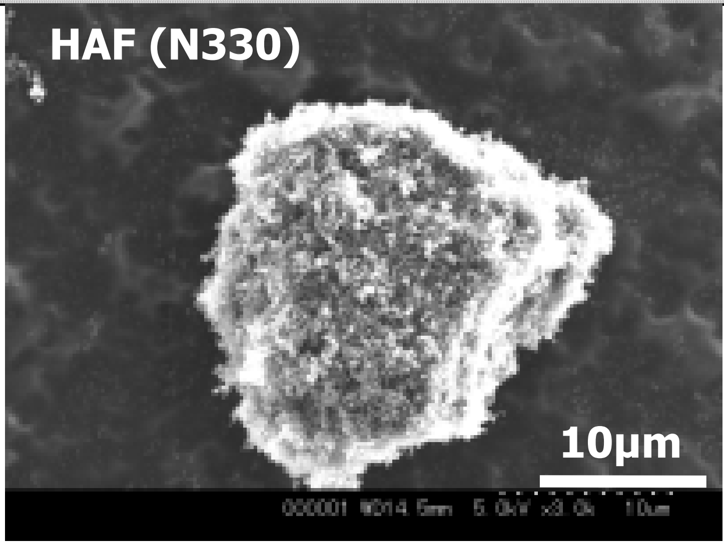
Unfilled NBR:Polymer Polarity

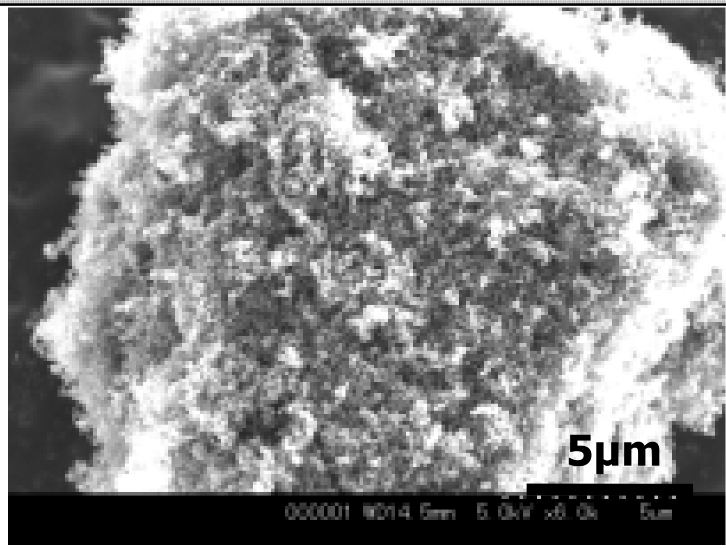


Volume inflation per hydrogen content is constant for all NBR.

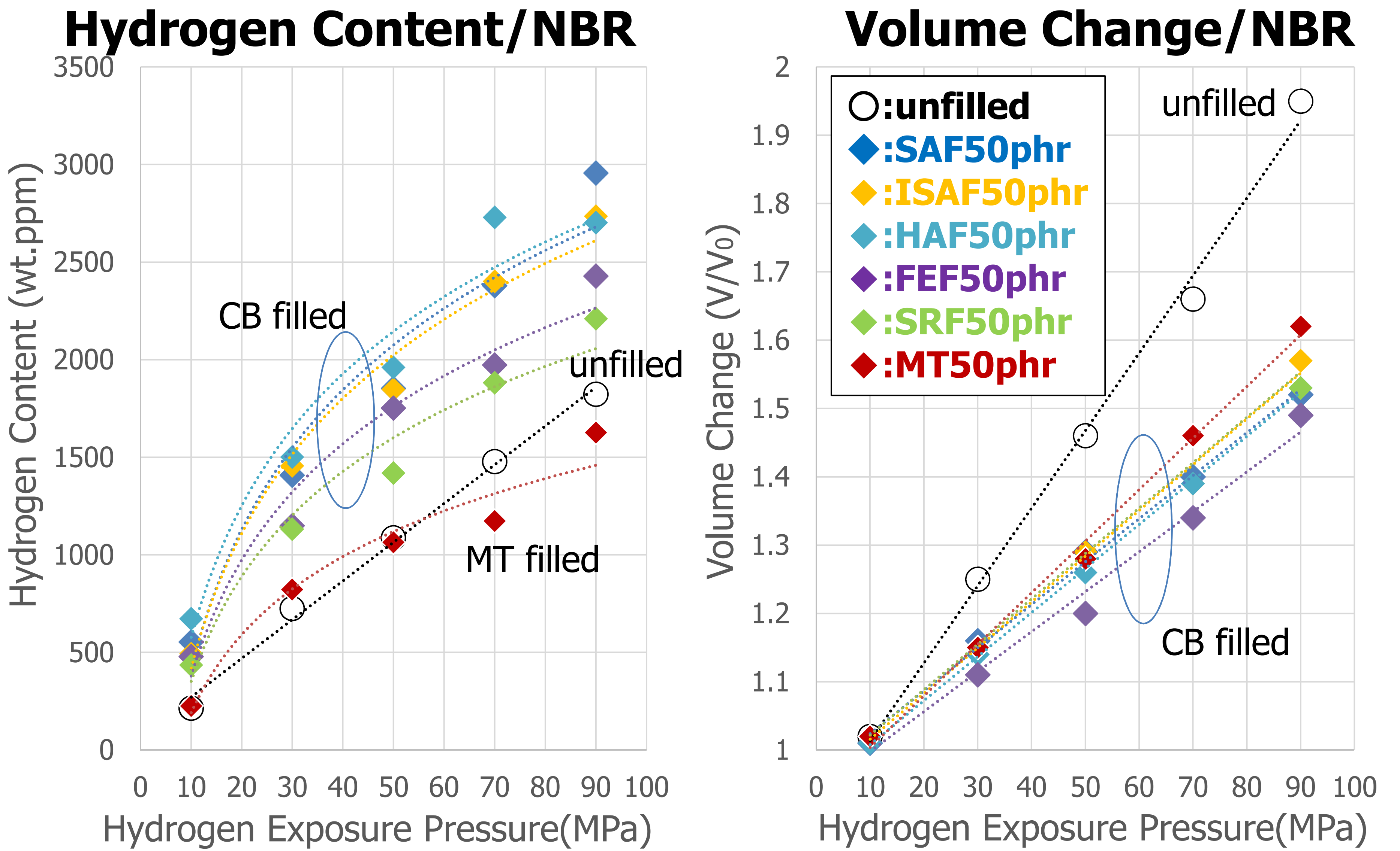
CB filled NBR:CB surface area

	SAF (N110)	ISAF (N220)	HAF (N330)	FEF (N550)	SRF (N774)	MT (N990)
Average Particle Size (nm)	**19**	**22**	**28**	**43**	**66**	**280**
Nitrogen Surface Area (m^2/g)	**142**	**119**	**79**	**42**	**27**	**7-12**
DBP Absorption ($cm^3/100g$)	**115**	**114**	**101**	**115**	**68**	**44**



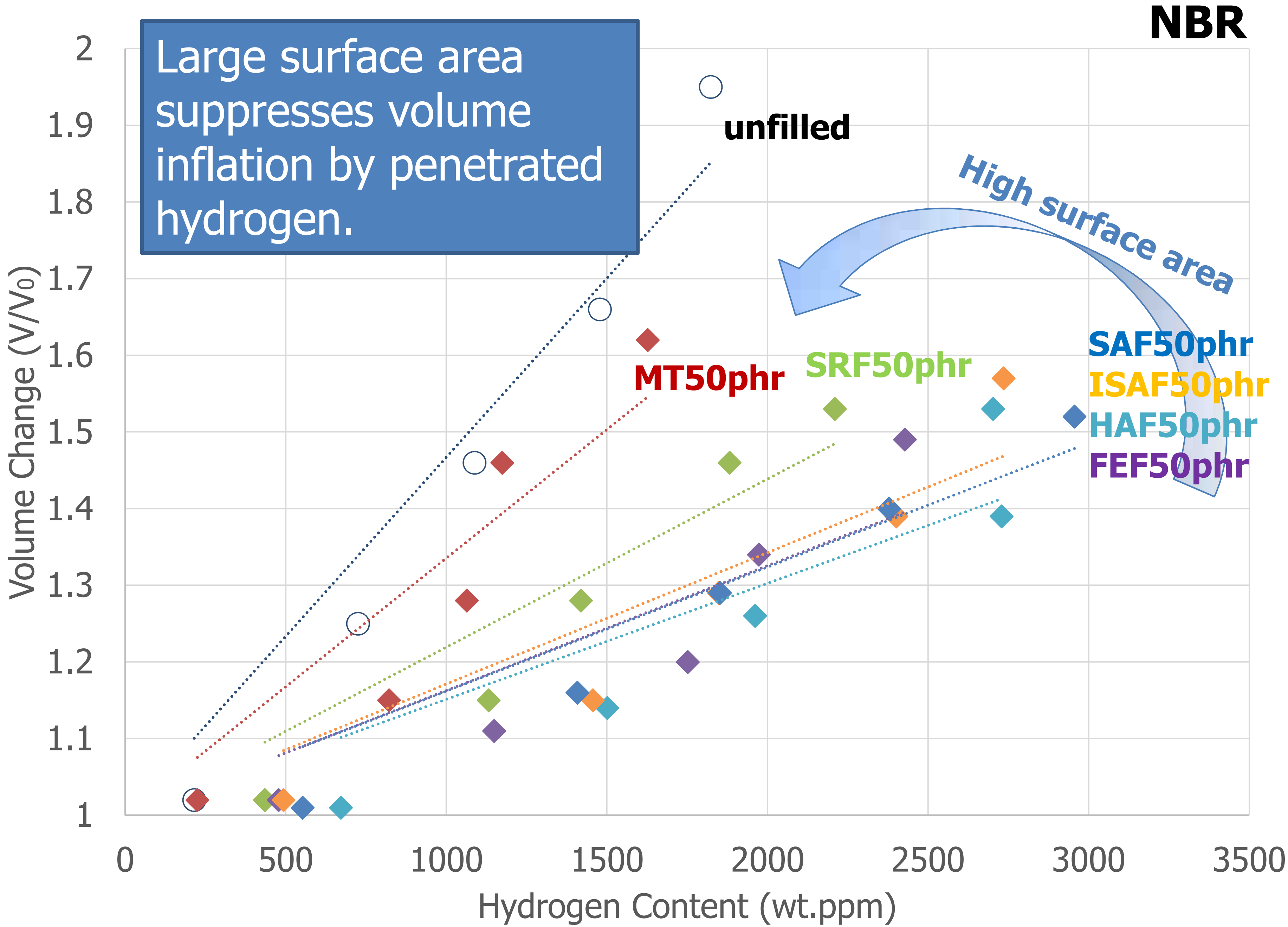


CB filled NBR:CB surface area

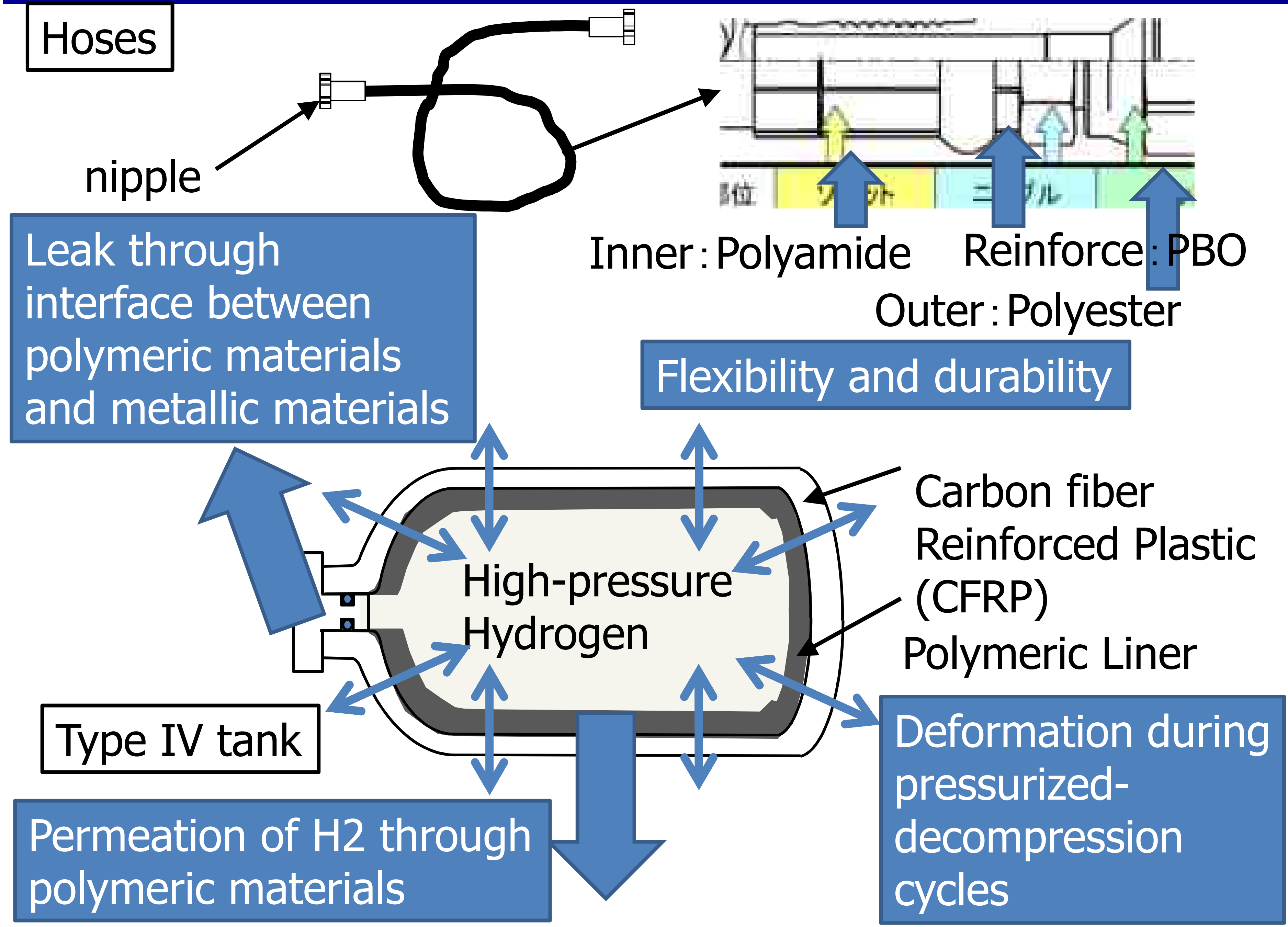


Carbonblack filled NBR's showed high hydrogen content and low volume inflation.

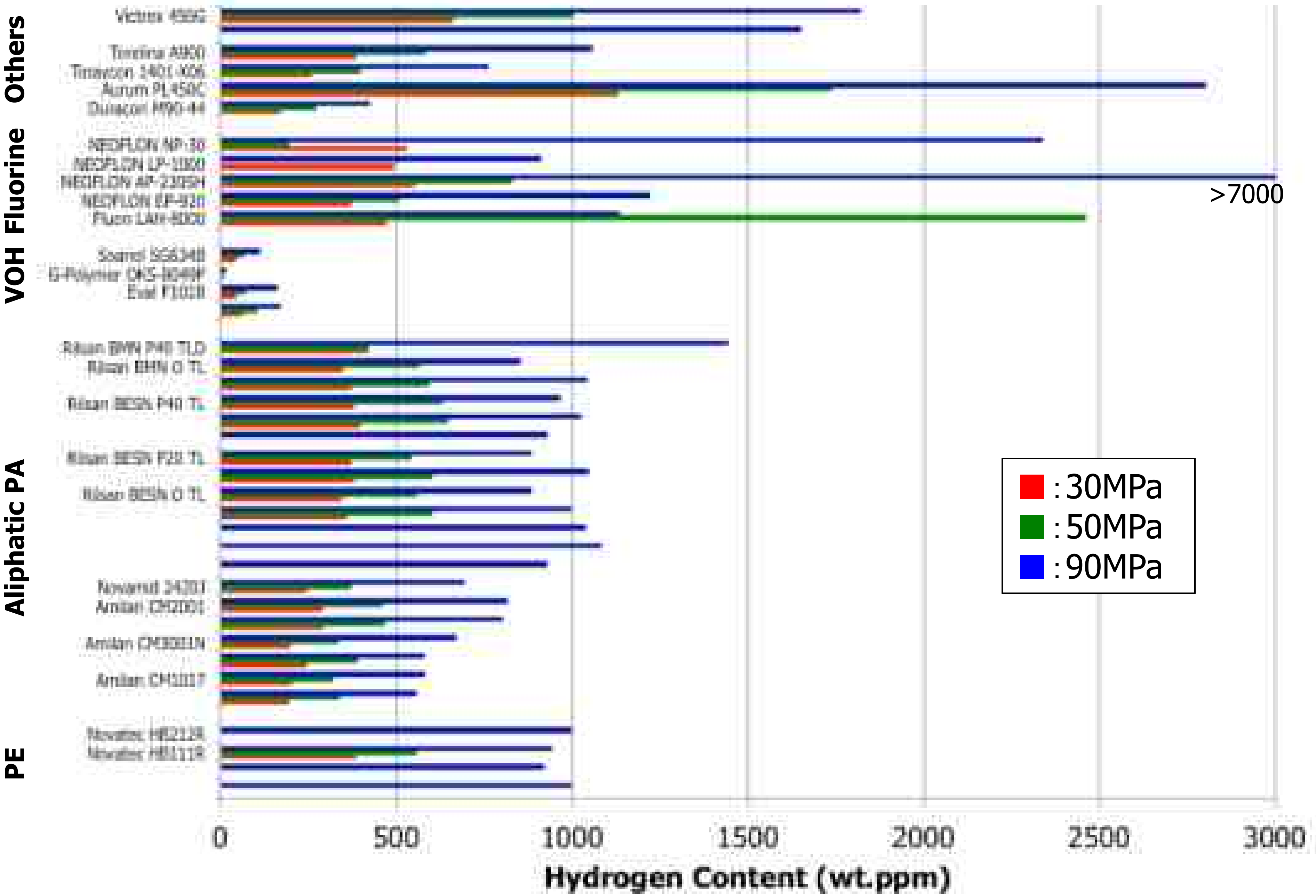
CB filled NBR:CB surface area



Issues on polymeric materials for tank and hose



Hydrogen Content of Polymeric Materials

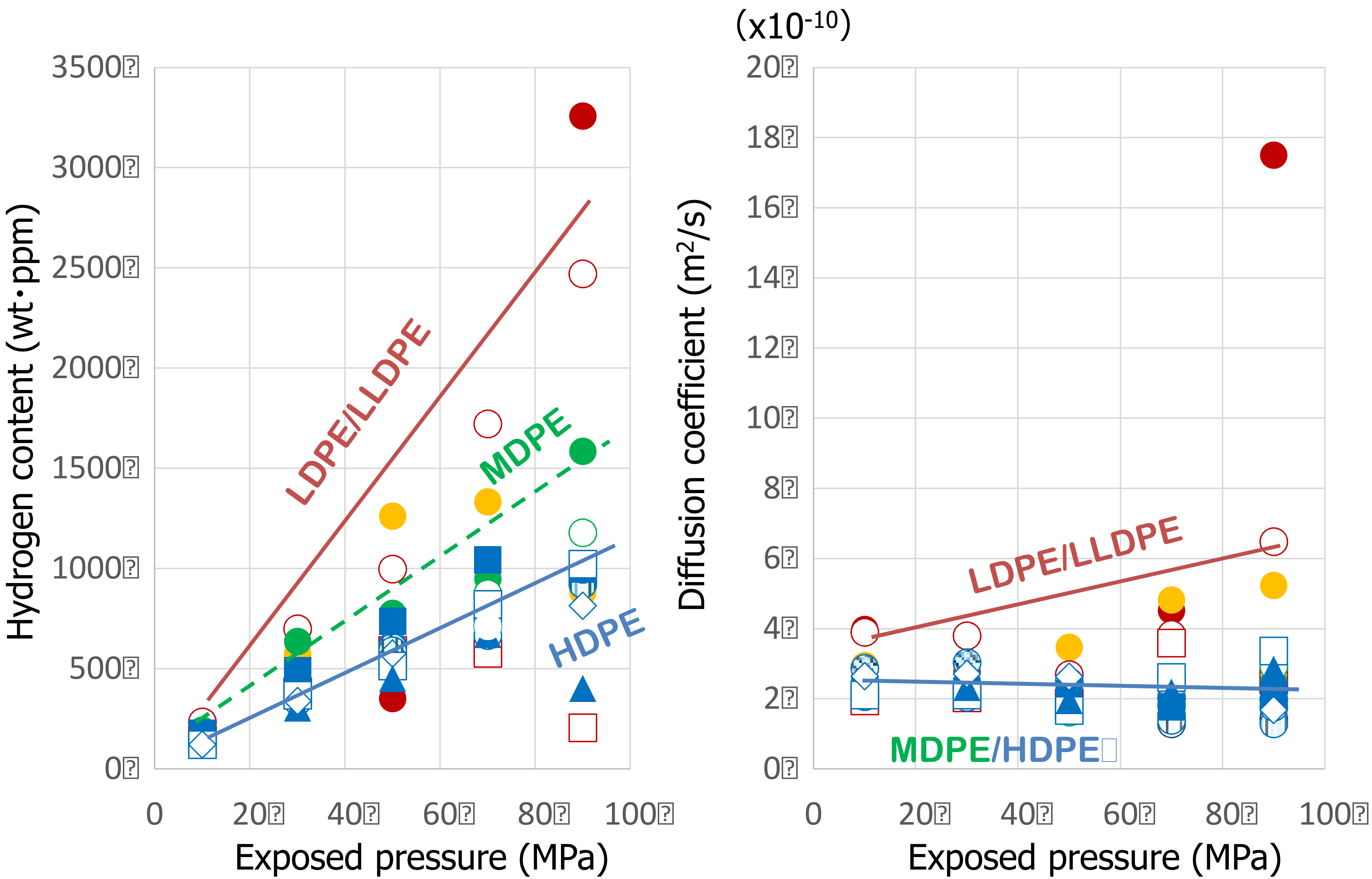


Polyethylene

Category		Type	Molding	χ^{WAXS}	χ^{DSC}	ρ
LDPE	Low density	NOVATEC LD ZE41K	Heat Press	44.4	42	0.917
LLDPE	Linear low density	NOVATEC LL UR951	Heat Press	43.8	36	0.916
UHMWPE	Ultra High Mw	SKF ECOWARE 1000	Heat Press	62.1	49	0.924
MDPE	Middle density	JPE PE80	Heat Press	73.4	62	0.934
HDPE	High density	NOVATEC HD HB111R	Heat Press	76.1	59	0.942
		NOVATEC HD HB111R	Heat Press	76.4	64	0.943
		NOVATEC HD HB111R	Blow	75.1	56	0.941
		NOVATEC HD HB212R	Heat Press	78.6	64	0.946
		JPE PE100	Heat Press	80.0	65	0.947
		Hi-ZEX 7000F	Injection	78.7	67	0.947

$|^{WAXS}$(%) : Degree of Crystallinity determined by Wide Angle X-ray Scattering
$|^{DSC}$(%) : Degree of Crystallinity determined by Differential Scanning Calorimetry
〉(g/cm^3) : Density determined by Archimedean method

PEの水素特性評価


Hydrogen content (wt・ppm)
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
100
Exposed pressure (MPa)
LDPE/LLDPE
MDPE
HDPE
(x10-10)
Diffusion coefficient (m2/s)
20
18
16
14
12
10
8
6
4
2
0
0
20
40
60
80
100
Exposed pressure (MPa)
LDPE/LLDPE
MDPE/HDPE

Summary

- Polymeric materials can be fractured by blisters and volume increment, which are originated from penetrated hydrogen.
- Volume change ratio is proportional to its hydrogen content. Carbon black can reduce the volume change of the compounds nevertheless their hydrogen contents are high.
- According to the results of model materials, O-rings for hydrogen equipment, such as breakaway device, are developed
- Liner materials of high-pressure hydrogen hoses and type IV tanks are required that low permeability of hydrogen, high durability for pressure cycles, good controllability of interface with metal materials.
- Database of elastomers for hydrogen equipment is now under discussion in the research group of the Society of Rubber Science and Technology, Japan.

Thank you very much for your kind attention.