水素膨潤状態における過酸化物架橋アクリロニトリルブタジエンゴムの放射光小角 X 線散乱法による構造解析

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燃料電池自動車の実用化に向け、高圧水素容器の安全設計に関する研究開発が推進されている。高圧水素容器のシール材としてゴム材料が用いられるが、高圧水素曝露したゴムは減圧後、溶解水素の影響により体積膨張し、はみ出し破壊・座屈破壊を伴う。体積膨張のメカニズムを明瞭化し、耐高圧水素シール材料の分子設計指針を確立することは、安全な水素エネルギー社会の実現のための重要な課題である。

本研究では、ゴム中に存在する高次構造の不均一性に着目し、水素曝露後の試料について、放射光 X 線を用いた X 線小角散乱測定により不均一構造のサイズ及び体積分率の経時変化を評価し、水素膨潤時の不均一構造と水素溶解量の相関について考察した。不均一構造解析を行うにあたって、ゴムの構造はゴム分子鎖の密集した領域（高密度相）と疎な領域（低密度相）の 2 相からなるという仮定に基づく、Debye-Bueche 式を適用した。

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Structural study of peroxide crosslinked acrylonitrile butadiene rubber in hydrogen swelling state by synchrotron small angle X-ray scattering

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Background for this study

Fuel cell vehicle(FCV) need high pressure hydrogen (70MPa).
High pressure hydrogen gas resistant seal is required.

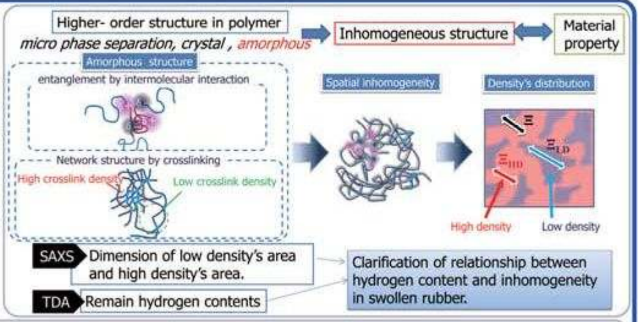
➡ Qualitative improvement for seal materials.

Establishment of design guideline for high pressure hydrogen resistant material

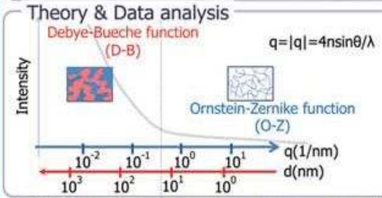
H_2 Overflow fracture

EPDM (Exposed by 100MPa/30℃/24h)

Hydrogen exposure ➡ volume expansion ➡ O-ring fracture



Theory & Data analysis



D-B

$$I(q)=\frac{I(0)}{\left(1+\Xi^2 q^2\right)^2}$$

O-Z

$$I(q)=\frac{I(0)}{1+\xi^2 q^2}$$

Curve fitting

$$I(q)=\frac{I_e}{I_0}\cdot(\Delta\rho)^2\varphi_{HD}\,\varphi_{LD}\,8\pi\,\Xi^3\left(\frac{1}{1+q^2\Xi^2}\right)^2$$

$$I_{abs}(q)=I_s(q)\cdot\frac{1}{I_0\cdot T\cdot\varepsilon\cdot V}$$

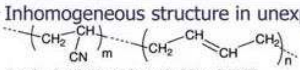
$$\Xi_{HD}=\frac{\Xi}{\varphi_{LD}},\ \Xi_{LD}=\frac{\Xi}{\varphi_{HD}}$$

➡ Identification of parameter

Tab. Parameter of theoretical function

I_e($cm^{-2}s^{-1}$)	Electron scattering density
$\Delta\rho$($1/cm^2$)	Scattering length density
V (cm^3)	sample volume
I_0($cm^{-2}s^{-1}$)	incident intensity
T	transmission coefficient
ε	detector efficiency

Inhomogeneous structure in unexposed NBR



Acrylonitorile Butadiene Rubber (**NBR**)

Tab. Chemical composition and physical property

ITEM	PO-0.15	PO-1.0	PO-1.6
NBR AN33.5% (Nipol 1042:Std)	100	100	100
Stearic Acid	0.5	0.5	0.5
Dicmyl Peroxide	0.15	1.0	1.6
Crosslink density (mmol/cm^3)	0.11	0.20	0.26

*Materials are supplied by Takaishi-Industrial co.,Ltd.
phr : per hundred rubber (g/rubber100g)

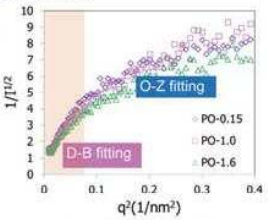


Fig A plot of $1/I^{-1/2}$ against q^2.

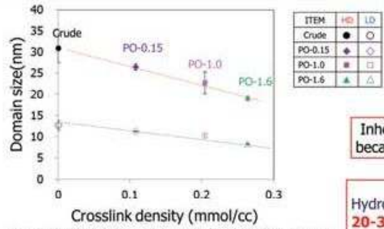


Fig relationship between domain size and crosslink density.

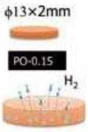
Domain size of inhomogeneous structure is correlated with crosslink density.

Inhomogeneities consisting of NBR became small ➡ uniform distribution

Hydrogen unexposed NBR's Ξ_{HD} and Ξ_{LD} is **20-30nm** and ca.**10nm** ,respectively.

Hydrogen exposure

- Pressure:90MPa
- Time:24hrs
- Temperature:30℃



After decompression

- Small Angle X-ray scattering(SAXS) NanoSTAR (Bruker AXS. Co., Ltd.)
- Thermal Desorption Analysis (TDA) JSH-201 (J-Science Lab. Co., Ltd.)
- Measurement of volume change Digital Vernier callipers

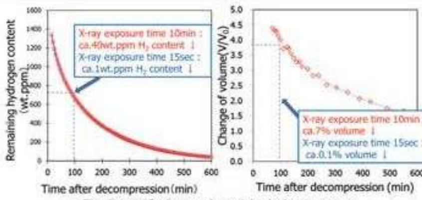
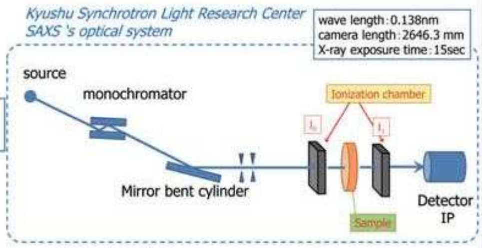


Fig change of volume and remaining hydrogen content.

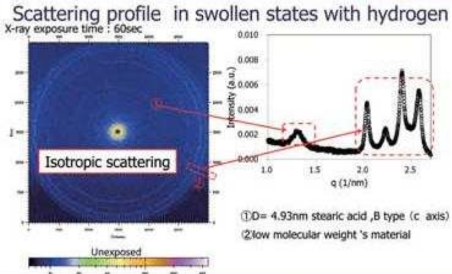
Precision of time division measurement

High intensity synchrotron radiation is required

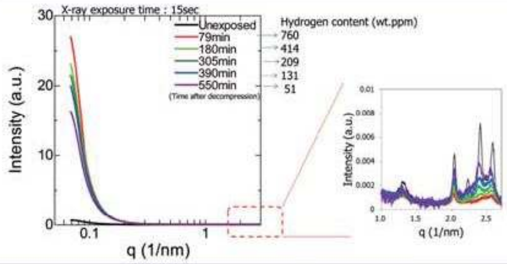


I_0: incident intensity
I_1: transmitted intensity
T : transmission coefficient(I_1 /I_0)

Scattering profile in swollen states with hydrogen



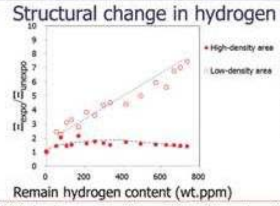
①D= 4.93nm stearic acid ,B type (c axis)
②low molecular weight 's material



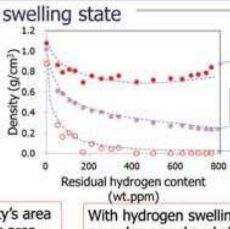
The cutoff of low q region (i.e. upper limit in which Debye-Bueche function is effective) is about q =0.2

After hydrogen gas decompression (with hydrogen swelling) , scattering intensity increased rapidly . The curve fitting was employed in terms of D-B zone.

Structural change in hydrogen swelling state



With hydrogen swelling , Ξ/Ξ_0 of low density's area increased larger than that of high density's area.



$$\rho_{HD}=\frac{W\cdot w_{HD}}{V\cdot v_{HD}}$$

$$\rho_{bulk}=\frac{W}{V}$$

$$\rho_{LD}=\frac{W\cdot w_{LD}}{V\cdot v_{LD}}$$

With hydrogen swelling , density of low density's area decreased and closed up to 0g/cm^3.

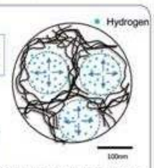


Fig Schematic image of rubber after hydrogen exposure

Summary

The morphology of spatial inhomogeneous structure in peroxide crosslinked NBR was observed by SAXS before and after hydrogen exposure.

- NBR have inhomogeneous structure oriented from network structure by crosslink and AN content . High density's domain size and low density's domain size is ca. 20nm and 10nm, respectively.
- In hydrogen swelling state, low density's area is growing up, and contrast against high density's area (polymer-rich phase) become remarkable.

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