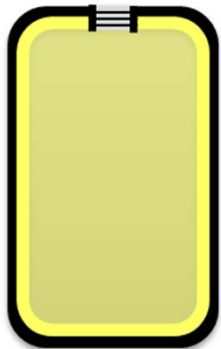# Degradation behavior of polymer materials in the high pressure hydrogen gas exposure

Polymer materials have an important role for the hydrogen storage cylinder. But it is not completely clarified how the high pressure hydrogen affects the polymer materials. The degradation behavior of the high density polyethylene molding exposed the high pressure H_2 gas is investigated by various analysis methods.
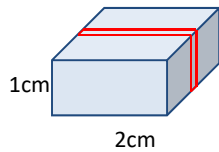
Schematic overview of the High pressure cylinder and the test sample

Type-4
Surface layer：CFRP, liner：Resin

The test specimen

1cm
2cm

Sample:
High density polyethylene molding before and after the exposure test.

Type-4 cylinders are more efficiency in manufacturing processes and lighter than the aluminum lined type-3.

・ Optical micrograph of the test specimen section
・ Bending strength of the test specimen

Before the test
5mm
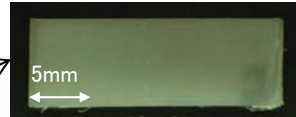
After the test
2.6mm
3.9mm
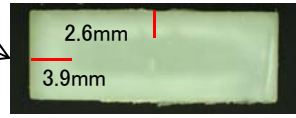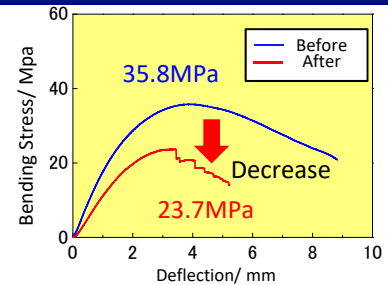
The area from the surface to about 4mm in depth whitened by the exposure test.

35.8MPa
Decrease
23.7MPa

The bending strength was decreased and irregular stress liberation behavior was observed in the exposure sample.

Sub- μm cavities and defect structure may be formed.
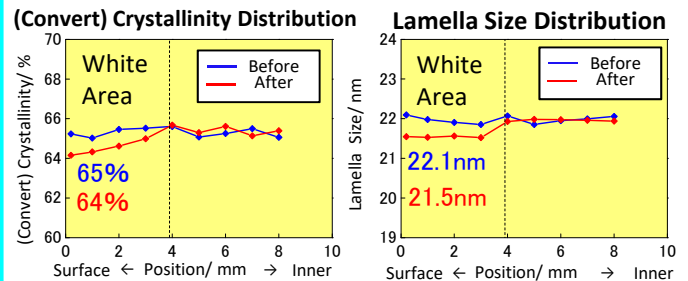The analysis focused on the crystal structure is performed using by following methods.

Crystal structure analysis by DSC and XRD

DSC curves

EXO.

Crystallinity
76%
75%

ENDO.
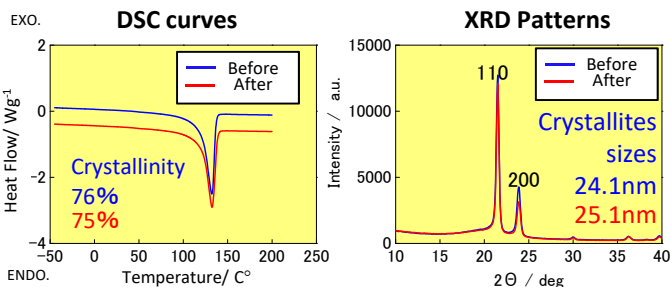
The crystallinity was slightly decreased after the test.

XRD Patterns

110
200

Crystallites sizes
24.1nm
25.1nm

The crystallites sizes became slightly larger after the test.

Crystal structure distribution analysis by Raman spectroscopy

Surface → Inner

(Convert) Crystallinity Distribution

White Area
65%
64%

Surface ← Position/ mm → Inner

Lamella Size Distribution

White Area
22.1nm
21.5nm

Surface ← Position/ mm → Inner

The (convert) crystallinity was decrease and lamella sizes became smaller in the white area.

・ Molecular Weight Distribution（MWD）by GPC
・ Free Volume Distribution by PALS

MWD

分子量
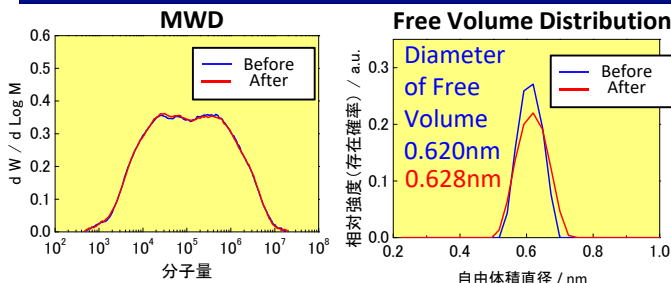
The MWD was not change before and after the test.

Free Volume Distribution

Diameter of Free Volume
0.620nm
0.628nm

自由体積直径 / nm

The free volume sizes became slightly larger after the test.

	Bending Strength	DSC	XRD
		Crystallinity	Crystallites size
Before	35.8MPa	76%	24.1nm
After	23.7MPa	75%	25.1nm

	Raman		GPC	PALS
	(Convert) Crystallinity	Lamella Size	Weight-average Molecular Weight M_w	Diameter of Free Volume
Before	65.2%	22.1nm	611000	0.620nm
After	64.2%	21.5nm	607000	0.628nm

After high pressure H_2 exposure test, the surface of the molding whitened and the bending strength was decrease. In the white area, the crystal and amorphous structure changed slightly. It is concluded that the changes of the appearance and the strength were caused by generation sub- μm cavities and defect structure.

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