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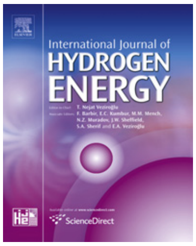

Evaluation of the change in chemical structure of acrylonitrile butadiene rubber after high-pressure hydrogen exposure

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ABSTRACT

The influence of high-pressure hydrogen on the chemical structure of organic materials is essential for designing suitable materials for the safe and efficient use of hydrogen. In this paper, we clarify the cause and mechanism of “explosive failure by decompression” (XDF) in rubber used under high-pressure hydrogen circumstances, and the chemical structure of acrylonitrile butadiene rubber (NBR), which is commonly used for O-rings, was analyzed after exposure to hydrogen at 100 MPa. Solid-state nuclear magnetic resonance (NMR) and liquid-phase NMR for ^{1}H and ^{13}C, as well as infrared and Raman spectroscopy, were employed for the evaluation. The results show no evidence of structural changes in NBR such as hydrogenation of the olefinic bonds in butadiene or of the cyano groups in acrylonitrile.

1. Introduction

The shortage of energy resources and the deterioration of the environment caused by the excessive dependence on fossil fuels are serious and urgent issues all over the world. Utilization of hydrogen as a next generation energy carrier is expected to solve these problems. For safe and efficient storage and transfer of hydrogen, it is necessary to analyze the influence of high-pressure hydrogen gas on vessels, pipes, and sealing, and to design materials appropriate for the particular purpose.

We have previously evaluated the influence of hydrogen on rubber after hydrogen exposure with the aim of developing rubber materials suitable for sealing high-pressure hydrogen storage vessels and delivery systems [1,2]. For example, an accumulator O-ring for 100 MPa hydrogen gas failed after twenty compression and decompression cycles. We have reported that the fracture mechanism in the O-ring was explosive failure by decompression (XDF) in terms of hydrogen dissolved in the rubber materials [3]. Fig. 1 shows an example of acrylonitrile butadiene rubber (NBR) material with XDF.

Generally, macromolecules such as rubber and plastic are well known to decompose through exposure to heat, mechanical energy, light, high-energy radiation, microbes, and solvents [4]. From the view point of an interaction with a gas, oxidization in the atmosphere or ozone is commonly known. Hydrogen, being a reducing gas, progresses hydrogenation in the presence of various catalysts so commonly as the reaction system has been established as an independent

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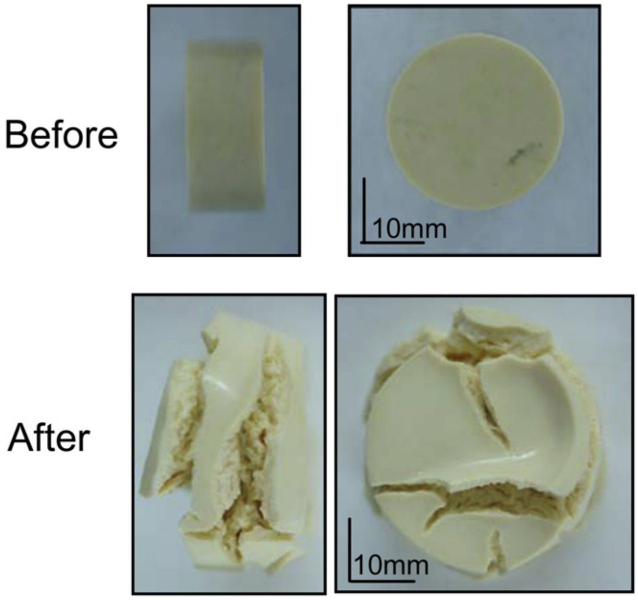

Fig. 1 – A photo of XDF in rubber (NBR) after 100 MPa hydrogen gas exposure.

branch of organic synthesis [5]. Under high-pressure conditions, an unexpected reaction could progress because pressurization supplies energy exceeding the activation energy needed for activation of rubber molecules to the transition state. Bhattacharjee et al. [6] reported that more than 70% of NBR converted into hydrogenated NBR (HNBR) under a hydrogen pressure of less than 1 MPa with a rhodium catalyst. It is also known that the ultimate strength of completely hydrogenated HNBR is a factor of 12 times larger than NBR. Thus, hydrogenation of NBR greatly affects its mechanical properties.

The purpose of this study is to determine the conditions under which a change in the chemical structure of rubber materials employed for high-pressure hydrogen seals will occur during high-pressure hydrogen operation. The state of degradation of the rubber should be evaluated chemically as well as physically to determine the cause of XDF. It is important to understand chemical degradation by high-pressure hydrogen for a lifetime assessment of rubber sealing materials. To do this, the chemical structure of rubber that had failed due to XDF after high-pressure hydrogen exposure was analyzed. The degree of hydrogenation in the NBR was evaluated precisely by solid-state nuclear magnetic resonance (NMR).

As the vulcanized NBR that was used for this study is insoluble in most common solvents for NMR measurements, it was difficult to obtain high-resolution spectra for completely dissolved specimens in liquid-phase NMR, apart from the cases of “latex ^{13}C NMR” for natural rubber, as Kawahara et al. [7,8] have reported, and high-speed magic angle spinning (MAS) solid-state NMR. In this study, we employed swollen state NMR with the specimen swollen by a solvent and used for liquid-phase NMR in which the dipole–dipole interaction is countervailed and the anisotropy of the chemical shift is standardized. Consequently, we could obtain high-resolution spectra. The resolution of solid-state NMR is not as high as that of liquid-state NMR, but it was employed mainly for the ^{1}H analysis to evaluate hydrogenation in NBR by taking advantage of its high reliability in the area values in the spectra. Liquid-phase NMR is not adequate for the area rate calculation as the resonance of the eluted substances, such as unreacted vulcanization accelerators, has a much higher resolution than swollen NBR and the process can disturb the calculation.

2. Experimental section

2.1. *Materials and experimental methods*

NBR (Zeon Co. NIPOL 1042) with an acrylonitrile (AN) content of 33.5% was used to prepare the rubber composite sample. The sample was prepared by mixing NBR, 2,2′-benzothiazyl disulfide (MBTS), bis(dimethyl thiocarbamoyl) disulfide (TMTD), stearic acid, zinc oxide, and sulfur according to the ratio given in Table 1.

A sheet sample 2 mm thick and a cylindrical sample ø29 mm × 12.7 mm were vulcanized in a mold, and the specimens were cut out from these samples. The samples were then cleaned with purified water and installed into a pressure vessel to be exposed to hydrogen gas. The interior of the vessel was depressurized to less than 9 Pa and was purged with 0.5 MPa nitrogen gas prior to hydrogen exposure. The exposure was conducted using 99.99% hydrogen gas under 100 MPa in a pressure vessel for 65 h at 30 °C. Before removing the specimens, the vessel was purged five times with 0.5 MPa nitrogen gas. The exposed specimens after more than 7 days were used to analyze the change in the chemical structure. The termination of hydrogen desorption in the specimens was ensured based on the result of the study using a thermal desorption analyzer [9].

2.2. *Equipment and conditions*

For the solid-state NMR (CMX 300 Infinity Plus/300 MHz: Varian-Chemagnetics), the specimen was placed in a ø4 mm sample tube with KBr and rotated at an MAS speed of 12,000 Hz (±20 Hz) to obtain the ^{1}H and ^{13}C NMR spectra. The standards used to determine the chemical shift were the silicon rubber methyl group (0 ppm) for the ^{1}H NMR spectra and the hexamethylbenzene methyl group (17.4 ppm) for the

Table 1 – Chemical composition (part by weight) and physical properties of vulcanized NBR.

NBR (Nipol 1042)	100
Stearic Acid	1
Zinc Oxide	5
Sulfur	1.5
2-Benzothiazolyl disulfide [MBTS]	1.5
Tetramethylthiuram disulfide [TMTD]	0.5
Hardness	A52
Density (g/cm^{3})	1.0355
Elastic modulus, E (MPa)	1.7
Nominal fracture strength σn (MPa)	2.0
Stretch at fracture, λF	4.3