Inhomogeneity in acrylonitrile butadiene rubber during hydrogen elimination investigated by small-angle X-ray scattering

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ABSTRACT

To understand the early stage of explosive decompression failure of rubber materials after high-pressure hydrogen exposure, the hydrogen elimination process of hydrogen-saturated peroxide-vulcanized acrylonitrile butadiene rubber (NBR) was investigated by small-angle X-ray scattering. The results were analyzed by the Debye—Bueche equation. Hydrogen-containing NBR samples exhibit a two-phase system with a clear interface, and the low-density phase of NBR samples is considered to be submicron-scale voids. The dimension of the voids in NBR becomes larger with decreasing cross-link density. The inflation of the voids in terms of the penetrated hydrogen contributes to the bulk-volume inflation after decompression. Estimated number densities of voids in the exposed NBR samples were almost constant. Judging from this, the voids in rubber samples after decompression are generated from precursors originally existing in the matrix, which are considered to be the low-density phase, which is attributed to the inhomogeneity of the cross-link density.

Introduction

The development and progress of science and technology in recent years have created several problems, such as global warming, caused by greenhouse gas emissions and the depletion of fossil fuels. Renewable energies, such as solar and wind power, are possible solutions to these problems. However, these renewable energies show large fluctuations in energy production, and it is necessary to store the produced renewable energy to compensate for their output fluctuation. Hydrogen energy is one candidate for the storage of renewable energy. In terms of converting energy to hydrogen as a secondary energy, it is much easier to store and transfer than electricity. Furthermore, hydrogen energy has attracted attention as a clean energy that does not emit carbon dioxide and only water is emitted during consumption. Fuel cell systems using hydrogen as the energy carrier have a high-energy efficiency [1]. Hydrogen has a high weight energy density as a fuel; however, its volume energy density is extremely low, i.e., 0.01 GJ m^{-3}, because it is a gas at ordinary temperature and normal pressure. For practical applications, it is necessary to improve its volume energy density. One reasonable method is to pressurize the gaseous hydrogen [2] [3]. For example, the volume energy density of 70 MPa hydrogen is 7 GJm^{-3} at

ordinary temperature. This value is equivalent to those of conventional liquid fuels.

However, high-pressure hydrogen involves the risk of leakage throughout the production, transport, and storage processes. It is important to ensure safety in order to establish hydrogen energy systems. In the case of fuel cell vehicles, the practical storage pressure for fuel hydrogen gas is 70 MPa [4] [5]; thus, high-performance sealing technology for high-pressure hydrogen gas is required. During the practical use of rubber materials for hydrogen gas seal, high-pressure hydrogen exposure causes explosive decompression failure (XDF), i.e., "Blister fracture" and overflow fracture or buckling fracture of sealing devices caused by volume expansion of rubber materials [6]. In order to establish guidelines for the molecular design of high-performance sealing materials, pursuing the mechanism of XDF in terms of the structural and volumes change in rubber seal materials caused by hydrogen exposure is a high priority. The possibility of chemical structure changes has been examined and was ruled out by Fujiwara and Nishimura [7] [8]. They analyzed the chemical structure of NBR after exposure to hydrogen at 100 MPa by solid-state nuclear magnetic resonance (NMR) and liquid-phase NMR for ^{1}H and ^{13}C, as well as infrared and Raman spectroscopy. The results showed no evidence of chemical structure changes in NBR such as hydrogenation of the unsaturated bonds in butadiene or hydrogenation of the cyano groups in acrylonitrile. Yamabe and Nishimura reported that hydrogen penetrates into sealing rubber materials as hydrogen molecules. After decompression, the penetrated hydrogen is eliminated from rubber materials. During the hydrogen elimination process, hydrogen molecules in the rubber materials cause XDF [9]. They reported the results of observations by acoustic emission method and atomic force microscope, for ethylene propylene rubber (EPDM) after hydrogen exposure [10], and they concluded that low-strength sites related to inhomogeneity of the cross-link density in the rubber were the origin of the XDF.

The relationship between XDF and hydrogen exposure pressure and decompression rate was investigated by Jaravel and Castagnet [11]. They established a numerical simulation model for XDF of rubber materials and reproduced the XDF behavior of EPDM using the model. Their model is based on the supposition that rubber composites originally have a bubble, and the initial bubble is supposed to be inflated by the penetrated hydrogen and leads to fracture. This model can reproduce XDF behavior including the decompression rate dependence of XDF. Unfortunately, their model does not mention the origin of the initial bubble, which is an important information for the composites' design.

However, there is no evidence for the very early stage of XDF behavior, which requires submicron-scale observation. Regarding submicron-scale observation of rubber materials, several studies employing small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) have been reported. Shibayama et al. reported that the scattering function of polyacrylamide gels is the sum of the scattered intensity from a corresponding polymer solution (Lorentz function) and the excess scattering (Square-Lorentz function, so-called " Debye–Bueche function") [12]. The excess scattering is due to the inhomogeneity of the network-chain density. Ikeda et al. applied the combination of this function to sulfur-vulcanized

isoprene rubber swelled by toluene-d_8 [13] and peroxide-vulcanized natural rubber swelled by toluene-d_8 [14]. Ono et al. reported that NBR has inhomogeneity of mobility by pulsed NMR method [15]. The mobility of chain molecules does not change in the hydrogen-containing state [16].

In order to understand the very early stage of XDF, investigation of submicron-scale morphological structure change during the hydrogen elimination process is required. In this study, SAXS was applied for observation of submicron-scale voids in peroxide-vulcanized acrylonitrile butadiene rubber (NBR) composites during hydrogen elimination to form hydrogen-saturated rubber materials after high-pressure hydrogen exposure.

The results were analyzed by the Debye–Bueche equation in order to understand the network-chain density change in the hydrogen-containing NBR samples due to hydrogen elimination. The effect of the cross-link density of the vulcanized NBR compounds on the behavior of submicron-scale voids during the hydrogen elimination process after high-pressure hydrogen exposure was also investigated.

Experimental section

Sample preparation

NBR (ZEON Corporation NIPOL 1042, acrylonitrile (AN) content of 33.5%), stearic acid, and dicumyl peroxide were mixed by using a 14-inch double-roll mill with a circulation cooling system manufactured by Kansai Roll Co. Ltd. The chemical composition of the samples is shown in Table 1. The compounds were vulcanized in a mold into sheets of 2 mm in thickness at 170 °C for 5 min by a 37 ton compression molding press. The specimens for measurements were prepared by cutting from the sheet.

Hydrogen exposure procedure

Hydrogen exposure was conducted using 99.99% hydrogen gas under 90 MPa in a pressure vessel at 30 °C for 24 h. Disc-shaped specimens (diameter: 13 mm; thickness: 2 mm) were cut from the vulcanized sheet and exposed to 90 MPa hydrogen gas in a high-pressure vessel. The high-pressure hydrogen gas was immediately released after a 24 h exposure at a decompression rate of more than 90 MPa/min.

Measurement

SAXS measurement
SAXS measurements of the hydrogen exposed vulcanized NBR samples were performed at room temperature by

Table 1 – Chemical composition of NBR samples with different cross-link densities (phr: per hundred rubber).

ITEM	PO0.15	PO0.5	PO1.0
NBR AN33.5% (Nipol 1042:Std)	100	100	100
Stearic Acid	0.5	0.5	0.5
Dicumyl Peroxide	0.15	0.5	1.0