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Penetrated hydrogen content and volume inflation in unfilled NBR exposed to high-pressure hydrogen—What are the characteristics of unfilled-NBR dominating them?

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ABSTRACT

A series of unfilled acrylonitrile butadiene rubber (NBR) composites, which consists of several types of NBR with acrylonitrile (AN) monomer unit ratio (X_{AN}) and sulfur or dicumyl peroxide (DPO) as a vulcanizer, were exposed to 90 MPa hydrogen gas to measure the saturated hydrogen content: C.H(0) and the volume change ratio when the sample volume is the maximum: V_{MAX}/V_0. The aim of this paper is to reveal the dominant characteristics for C.H(0) and V_{MAX}/V_0 of unfilled NBR composites. Mechanical properties, X_{AN}, the molecular weight of the number average molecular weight between the effective crosslinks (M_{ef}), the molecular weight between the chemical crosslink (M_C) and the fractional free volume (*FFV*) were employed to examine the relationship between the characteristics and C.H(0) and V_{MAX}/V_0 of the NBR composites. Judging from the results of the comparisons of C.H(0) and V_{MAX}/V_0 with X_{AN}, M_{ef}, M_C and *FFV*, it is revealed that C.H(0) and V_{MAX}/V_0 were dominantly correlate with *FFV* and M_C, respectively.

Introduction

Recently, practical use of Fuel Cell Vehicles (FCV) and Hydrogen Fueling Stations (HFS) have been started [1]. In a FCV, hydrogen gas is usually stored at approximately 70 MPa [2,3]. Because of small volume energy density of hydrogen gas, the hydrogen gas was compressed up to 70 MPa for storing in FCV. In the HFS, the hydrogen gas is pressurized by a compressor and stored in an accumulator at approximately 90 MPa [3,4]. Dispensing hydrogen to an FCV is driven by the differential pressure between the accumulator and the fuel tank of the FCV.

HFS consists of many devices, such as compressors, accumulators, valves, filters, pre-coolers, nozzles, to regulate the dispensing high-pressure hydrogen to the FCV. The connections of these devices requires the high-pressure hydrogen seal. Rubber materials are used as a seal device for the high-pressure hydrogen gas such as an O-ring. The rubber

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materials which is used as sealing devices of HFS are exposed to the high-pressure hydrogen up to 90 MPa. To design the appropriate rubber composites for the high-pressure hydrogen seal, it is important to understand the fracture or deterioration behavior of rubber materials under such the high-pressure hydrogen environment.

Fujiwara et al. tried to understand the chemical deterioration of the rubber materials under the high-pressure hydrogen of unfilled acrylonitrile butadiene rubber (NBR) composites. They reported that the high-pressure hydrogen exposure does not occur any chemical structure changes in NBR by NMR analysis [5,6]. Exposing the rubber materials to the high-pressure hydrogen, the hydrogen gas dissolves into the rubber materials and desorbs from them in the manner of diffusion after rapid gas decompression of the ambient high-pressure hydrogen [7]. The dissolved hydrogen gas in the rubber composites of an O-ring resulted from the high-pressure hydrogen exposure causes some types of damages, such as “bubbling”, “cracking”, “buckling” and “overflow”.

Bubbling and cracking: After the rapid decompression of the high-pressure hydrogen, considerable amount of bubbles begin to generate inside of the rubber materials and their sizes and numbers are increased with the elapse of time and, finally, the bubbles become an origin of crack. The cracks caused by the bubbles have been defined as “blister fractures” [7]. Yamabe and Nishimura revealed the bubble growth behavior using an optical microscope between 5.5 and 7.0 min after the decompression with transparent unfilled ethylene propylene diene rubber (EPDM) exposed to 10 MPa hydrogen gas at 30 °C. They also suggested the criterion of the crack initiation from bubbles using high-order Mooney-Rivlin equation as the inner pressure of the bubble for the crack initiation [7]. Koga et al. have directly observed initiation, growth and disappearance behavior of the bubbles in the transparent silicon rubber O-ring during the decompression process from 10 MPa hydrogen by the in-situ optical microscope observation for the high-pressure vessel equipped with an O-ring observation window [8]. Ohyama et al. attempted small angle X-ray scattering for NBR after 90 MPa hydrogen exposure to understand the early stage of blistering [9]. Jaravel et al. successfully reproduced the experimental results of the single bubble growth behavior in silicone rubber by their simulation model [10,11]. They conducted the in-situ photography observation of the silicone rubber under the condition of given saturation pressure and decompression rate to obtain experimental data. And then, they simulated the bubble growth using “diffuso-mechanical coupling” model —the bubble growth is resulted from the competition between the hydrogen diffusion from the inside of bubble to the rubber free surface through the matrix and the resistance of mechanical property of the rubber matrix against the triaxial loading. Concerning about the filled rubber composites, Fujiwara et al. reported that the blister fracture accompanies breaking the filler-gel structure in silica filled NBR proved by dynamic mechanical analysis and time domain NMR [6].

Buckling and overflow: Generally, a groove for install a rubber O-ring is designed taking into account the filled ratio and the squeeze ratio of the O-ring in the groove. The high-pressure hydrogen exposure causes the volume inflation of the rubber O-ring in the groove. Recently, the authors reported that a spherical unfilled NBR exposed to 30 MPa hydrogen gas at 30 °C begins inflation from the moment of decompression at the rate of 16 MPa/min until reaching the maximum volume and, subsequently, shrink with the elapse of time. The volume inflation corresponds to the volume inflation of hydrogen gas with the growth of bubbles and cracks [12]. Due to the O-ring inflation in the groove, the O-ring overflows from the groove which causes surface cracking or the O-ring rupture, which are called as “overflow” and “buckling”, respectively [13–15].

Above mentioned fractures of the O-ring are fatal failures for a high-pressure hydrogen seal. To avoid the failures, both appropriate design of the groove and of the rubber material for the O-ring are required. On the design of the rubber material for O-ring, saturated hydrogen content and volume inflation ratio of the rubber materials shall be *key* parameters—they shall be reduced. To design the rubber material with the target saturated hydrogen content and the volume inflation ratio, the correlation between the *key* parameters and the characteristics of the rubber material must be understood quantitatively.

Yamabe et al. reported that hydrogen gas solubility increases with the increase of carbon black (CB) content as the results of hydrogen gas permeation tests for the unfilled NBR, 25 phr (per hundred rubber) of CB filled NBR and 50 phr of CB filled NBR [7]. Yamabe et al. revealed that increasing of CB or silica (SC) content reduces the volume inflation and 60 phr of SC filled EPDM exhibits the lowest volume inflation judging from the result of 10 MPa hydrogen exposure to unfilled EPDM, 50 phr of CB filled, 25 phr of CB filled, and 60 phr of SC filled EPDM [16]. From the results of 0.7, 5, 10, 30, 50, 70, 100 MPa hydrogen exposure to unfilled and 50 phr of CB filled NBR, they also revealed that increase in exposure pressure increases “saturated penetrated hydrogen content” (hereinafter referred to as C.H(0)). C.H(0) and the volume of the rubber composites exhibits positive correlation although it is not linear relation [17].

As mentioned above, the enough information of the relationship between the *key* parameters – C.H(0) and the volume inflation – and the composites design parameters is not available. The correlation between the key parameters and the characteristics of rubber materials as the composites design parameters, e.g., filler types, filler size, surface area and content, types and quantities of plasticizers, polarity of polymer, crosslink density, are required. As well known, generally, commercial rubber products are composites of elastomers, fillers such as CB and/or SC, plasticizer, chemicals for crosslink and its acceleration, and so on. To reveal quantitative correlations among C.H(0), the volume inflation and characteristics of the rubber material which is a complex material, thus, the effect of the characteristics of the rubber material on the *key* parameters should be evaluated one by one, using a sample being modeled focusing on each characteristic.

This paper aims to reveal the dominant rubber characteristic to the key parameters –C.H(0) and the volume inflation after the high-pressure hydrogen exposure. As a first step, this paper focuses on the unfilled NBR to understand the effect of chain polarity and network structure. The authors designed and created a series of unfilled sulfur vulcanized NBR composites with several types of sulfur composition and different acrylonitrile (AN) monomer unit ratio (X_{AN}), and unfilled