Engineering Failure Analysis 35 (2013) 193–205

Contents lists available at SciVerse ScienceDirect

Engineering Failure Analysis

journal homepage: www.elsevier.com/locate/engfailanal

Failure behavior of rubber O-ring under cyclic exposure to high-pressure hydrogen gas

Junichiro Yamabe [a,d,*], Atsushi koga [b], Shin Nishimura [c,d]

[a] International Research Center for Hydrogen Energy, Kyushu University, Japan, 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan
[b] NOK Corporation, Japan
[c] Department of Mechanical Engineering, Faculty of Engineering, Kyushu University, Japan
[d] Research Center for Hydrogen Industrial Use and Storage (HYDROGENIUS), National Institute of Advanced Industrial Science and Technology (AIST), Japan

ARTICLE INFO

Article history:
Available online 24 February 2013

Keywords:
Fracture
Polymer degradation
Crack growth
Hydrogen
Failure analysis

ABSTRACT

This paper presents the effects of hydrogen pressure, ambient temperature and pressure cycle pattern on fracture behavior of O-rings moulded from a peroxide-crosslinked EPDM rubber with white reinforcing filler under cyclic exposure to high-pressure hydrogen gas. By using a developed durability tester which enables the O-rings to expose cyclically high-pressure hydrogen gas, pressure cycle tests were performed at hydrogen pressures ranging from 10 to 70 MPa and ambient temperatures ranging from 30 to 100 °C under two pressure cycle patterns (test frequencies). The cyclic hydrogen exposure caused cracks in the O-rings, and their crack damage became more serious with an increase in the hydrogen pressure and the ambient temperature. The serious crack damage under high temperature is believed to be due to degradation of mechanical properties with increasing ambient temperature. At a hydrogen pressure of 10 MPa, cracks (blisters) caused by bubbles formed from supersaturated hydrogen molecules after decompression were observed. At a hydrogen pressure of 35 MPa or more, a large volume increase of the O-rings was observed by swelling; then, its volume increase induced extrusion fracture of the O-rings in addition to blister fracture. The crack damage also became more serious with a decrease in test frequency. The effect of the test frequency on the crack damage of the O-rings is presumed to be attributed to time-dependent crack growth behavior of the EPDM rubber.

1. Introduction

As a result of the exhaustion of fossil fuels and the problems associated with global warming, fuel-cell systems that use hydrogen energy have received a considerable amount of attention. To achieve widespread acceptance by hydrogen-based energy society, it will be essential to ensure that its hydrogen energy is handled safely and reliably. Apparatus for handling hydrogen gas usually contains polymeric materials such as rubbers used in O-ring seals for preventing leakage of high-pressure gases as well as metal materials. In the case of rubbers, there is a particular danger of internal fracture (blister fracture), which occurs when high-pressure hydrogen gas is suddenly decompressed. Although there are several reports on the blister fracture of the rubber materials by high-pressure carbon dioxide, nitrogen, and argon gases [1–12], there have been no reports on the induction of this phenomenon by high-pressure hydrogen gas. We have previously shown that blister fracture occurred when cylindrical specimens (ϕ 29.0 mm × 12.5 mm) moulded from ethylene–propylene–diene–methylene linkage

* Corresponding author at: International Research Center for Hydrogen Energy, Kyushu University, Japan, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan. Tel.: +81 92 802 3904; fax: +81 92 802 3902.
E-mail address: yamabe@mech.kyushu-u.ac.jp (J. Yamabe).

1350-6307/$ - see front matter
http://dx.doi.org/10.1016/j.engfailanal.2013.01.034

(EPDM) rubber and acrylonitrile–butadiene rubber (NBR) filled with carbon black or silica fillers were exposed to hydrogen gas at up to 10 MPa, and investigated the effects of the strength properties and the hydrogen concentrations of the rubber materials on their blister fracture behavior [13,14]. As a result, it was clarified that high-pressure hydrogen gas induced blister fracture, and the blister damage of the rubber materials became slighter with a decrease in their hydrogen concentration and an increase in their Young's modulus and tensile strength. However, the fracture behavior of O-rings, which represent the actual form in which rubber materials are used, has not been fully evaluated at hydrogen pressures from 35 to 70 MPa and ambient temperatures from −60 to 100 °C, which correspond to those present in fuel-cell systems. The durability of rubber O-rings used as seals in high-pressure hydrogen service is considered to be governed not only by the properties of the rubber materials themselves, but also by environmental conditions such as hydrogen pressure and ambient temperature [1]. Therefore, the actual durability of such O-rings needs to be comprehensively evaluated under the environmental conditions to which they are likely to be exposed during service.

With this background, pressure cycle tests of O-rings moulded from a peroxide-crosslinked EPDM rubber filled with white reinforcing filler were performed at hydrogen pressures ranging from 10 to 70 MPa and ambient temperatures ranging from 30 to 100 °C under two pressure cycle patterns by using a developed high-pressure hydrogen durability tester, which enables the O-rings to expose cyclically high-pressure hydrogen gas at the maximum pressure of 90 MPa and ambient temperatures ranging from −60 to 100 °C. Then, the effects of the hydrogen pressure, the ambient temperature and the pressure cycle pattern on crack damage of the O-rings were elucidated from observations of cracks by optical microscopy (OM). Based on observations of fracture surfaces by scanning electron microscopy (SEM) and stress analysis by the finite element method (FEM), the mechanism of crack initiation and growth behavior of the O-rings was also investigated.

2. Materials, specimens and experimental methods

2.1. Material and specimens

An EPDM rubber, which was added to white reinforcing filler (90 phr, parts per hundred rubber) and peroxide (2.5 phr), was prepared. The durometer hardness and density were A70 and 1.30 g/cm^3, respectively. The glass-transition temperature (T_g) was determined as −50 °C by dynamic mechanical analysis (DMA). An O-ring specimen at a cross-sectional diameter of 3.5 mm and an inner diameter of 11.9 mm, sheet specimens at a thickness of 0.7 mm or 2 mm, and a cylindrical specimen at a diameter of 29.0 mm and a thickness of 12.5 mm were moulded from the EPDM rubber. These specimens were subjected to pressure forming at 150 °C for 30 min as a primary vulcanization treatment; a subsequent secondary vulcanization was conducted in an oven at 120 °C for 120 h.

2.2. Tensile test of sheet specimen and measurement of volume increase of O-ring specimen by swelling

A dumbbell-shaped specimen (type 3) [15] was prepared from the sheet specimen with 2 mm thickness and was tested at a cross-head speed of 500 mm/min in air at ambient temperatures of 0, 30 and 100 °C.

Time-dependent volume changes in O-rings were observed by using a densimeter. The O-rings were exposed to hydrogen pressures ranging from 5 to 70 MPa and an ambient temperature of 30 °C for 24 h. After decompression, their volume changes were measured in air at room temperature (25 °C). In order to measure the volume change after decompression as soon as possible, the O-rings were exposed to hydrogen gas at an ambient temperature of 30 °C.

2.3. Pressure cycle test by durability tester

Fig. 1a shows a schematic illustration of the high-pressure hydrogen durability tester developed. Hydrogen gas at 5 MPa was compressed to 95 MPa by compressor; then its pressured hydrogen gas was once accumulated in the pressure accumulator. After that, its high pressure hydrogen gas was cyclically supplied to eight O-ring holders installed with O-rings.

Fig. 1b shows the details of the installation of the O-rings. The squeeze ratio, which is the ratio of the diameter of the O-ring with squeezing to that without squeezing, was 16%. The recommended squeeze ratio ranges from 8% to 30%. The hydrogen penetrates from the inside surface of the O-ring through to its outside surface. This tester can be operated at hydrogen pressures ranging from 6 to 90 MPa and ambient temperatures ranging from −60 to 100 °C using a gas compressor and a temperature chamber operated by heat media.

Fig. 1c shows pressure cycle patterns. The pressure cycle tests were performed under two test frequencies (1 min/cycle and 160 min/cycle) at the maximum hydrogen pressures from 10 to 70 MPa and ambient temperatures from 30 to 100 °C. The minimum hydrogen pressure was nearly zero despite the pressure cycle patterns. Hereafter, the maximum hydrogen pressure is simply referred to as a hydrogen pressure, which is denoted by p.

2.4. Observations of crack morphology and fracture surfaces

After specific number of cycles, appearances and cross sections of O-rings were observed by OM. The fracture surfaces of cracks were observed by SEM.