



# Ozone degradation of vulcanized isoprene rubber as a function of humidity



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## ABSTRACT

Ozone degradation of vulcanized isoprene rubber was investigated by changing atmospheric humidity. Ozone exposure test of the vulcanized isoprene rubber was carried out with 50 ppm ozone at 40 °C, for 48 h under relative humidity (RH) between 20 and 90%, after a strain of 0.2 stretching. The degradation of the rubber was assessed by morphology observation with digital microscopy and rubbing test with a white swab. Black powders appeared on the surface of the rubber after ozone exposure test at more than 50%RH, while they did not at less than 50%RH. The severe ozone degradation of the rubber under high humidity condition was attributed to a generation of hydroxyl radical due to a reaction of water vapor and ozone.

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## 1. Introduction

Ozone degradation of vulcanized rubbers is well known to be a cause of deteriorations and serious troubles of rubber products [1–3]. For instance, ozone in the atmosphere attacks carbon-carbon double bonds of diene rubbers such as natural rubber (NR), isoprene rubber (IR), butadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), chloroprene rubber (CR) and so forth [4]. The reaction of ozone with the diene rubbers may generate molozonide as an intermediate, which is converted to carbonyl group and carbonyl oxide group [4]. The carbonyl oxide group may further react with the carbonyl group and the carbonyl oxide group to yield ozonide, homopolymer and polyoxane, respectively [4]. These reactions proceed on the surface of the rubbers as an ozonide layer, in which crack propagation takes place [5–8].

The ozone degradation of vulcanized rubbers is inevitably assessed at 40 °C under low humidity condition of less than 65%RH,

according to international standard, ISO1431, “Rubber, vulcanized or thermoplastic - Resistance to ozone cracking – Part 1: Static and dynamic strain testing”. Ozone cracks, which appear on the surface of the rubbers, are usually measured by visual observation, after ozone degradation. In this case, size and number of the ozone cracks are measured as an index of the ozone degradation. The rubber products, certificated according to ISO1431, are allowed to be distributed for commercial trades in the world market.

In the last decades, however, a lot of serious troubles have been reported for the rubber products in use, even though the products were certificated by ozone exposure test according to ISO1431. For instance, the rubber gasket made of natural rubber/ethylene propylene diene rubber (NR/EPDM) used for a hatch cover of a cargo ship was significantly degraded with ozone, when the ship plowed the ocean across the equator. The difference of the environmental condition between ISO1431 and the cargo ship going across the equator may be attributed to temperature and humidity; that is, near the equator, temperature and humidity inside containers, placed at upper row of a cargo compartment on a cargo ship, are reported to be about 70 °C and 80%RH, respectively [9–11]. Thus, it is necessary to investigate the effect of temperature and humidity on the ozone degradation of rubbers.

The effects of temperature and humidity on the ozone

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deterioration of rubbers have been qualitatively investigated in the last fifty decades [12–19]. For example, Aoyagi reported that the ozone degradation of vulcanized BR was significantly accelerated with 50 ppm ozone at 40 °C under 80%RH, compared with the ozone degradation at 40 °C under 10%RH [13]. In addition, Tu reported that size and number of microvoids and cracks on the surface of silicone rubber, vulcanized at high temperature, increased with increasing humidity, when it was exposed with 300 ppm ozone [14]. According to these results, the humidity may play a significant role in the ozone degradation of the rubbers, whereas the temperature may not. One may require understanding a molecular origin of the effect of humidity.

In the present study, we quantitatively investigate the effect of humidity on the ozone degradation of NR/EPDM gasket and isoprene rubber; that is, the effect of H<sub>2</sub>O in atmospheric air on the ozone degradation is precisely investigated. The ozone degradation under high humidity condition is compared with that under low humidity condition, in order to understand the mechanism of ozone degradation under high humidity condition. The proposed mechanism of ozone degradation is proved with synthetic isoprene rubber (IR) as a model, which was degraded at 40 °C under certain humidity conditions between 20 and 90%RH.

## 2. Experimental

### 2.1. Materials

NR/EPDM gasket for a hatch cover of a cargo ship was used in order to identify the cause of the ozone degradation. The structure of the gasket was a foamed rubber coated with a rubber lining.

Isoprene rubber (IR) used was IR2200 purchased from JSR Corp. Carbon black (CB) was Industry Reference Black (IRB#5, Columbian Chemicals Co.). Zinc oxide was purchased from Hakusutech Co., Ltd. Stearic acid was purchased from NOF Corp. Sulfur was purchased from Hosoi Chemical Industry Co., Ltd. Accelerator TBBS (*N*-(*tert*-Butyl)-2-benzothiazolesulfenamide) was purchased from Ouchi Shinko Chemical Industrial Co., Ltd. Two types of CB filled compound and pure gum compound were prepared according to standard formula of ISO2303 “Isoprene rubber (IR) – Non-oil-extended, solution-polymerized types – Evaluation procedures” (Table 1). The CB filled compound was prepared with a two-roll mill (HSU Feng Iron Factory) by mixing isoprene rubber with CB, sulfur, zinc oxide, stearic acid and TBBS. The pure gum compound was prepared by mixing isoprene rubber with sulfur, zinc oxide, stearic acid and TBBS. Vulcanization was carried out with a hot press (No.61-034, Ohtake Kikai Kogyo Co., Ltd.) by pressing the CB filled compound and the pure gum compound at 160 °C for 8 min (CB filled) and for 12 min (pure gum), respectively.

### 2.2. Ozone exposure test

The ozone exposure test was made with an ozone testing machine composed of an ozone generator (OZSD-0008D, Ebara Jitsugyo Co., Ltd.), a temperature-humidity chamber (SH-241, Espac Corp.) and an ozone monitor (EG-700EIII, Ebara Jitsugyo Co., Ltd.). Ozone exposure of the NR/EPDM gasket after a strain of 0.2 compressing the center was carried out with 50 ppm ozone at 40 °C under 80%RH for 72 h or at 80 °C under 20%RH for 168 h (no dew condensation). Ozone exposure of the CB filled IR vulcanizates or the pure gum vulcanizates were carried out with 50 ppm ozone at 40 °C for 48 h under certain humidity conditions between 20 and 90%RH after a strain of 0.2 stretching (no dew condensation). Crack propagation of the vulcanizates was observed by digital microscopy (VHX-2000, Keyence Corp.). The ozone degradation on the surface of the CB filled IR vulcanizates was assessed by rubbing the surface

of the vulcanizates with a white swab loaded between 2.5 and 3 N.

### 2.3. Measurements

Molecular structure on a surface of the vulcanizates was analyzed by attenuated total reflectance Fourier-transform infrared spectroscopy, ATR-FTIR (FTS-6000, Bio-Rad Laboratories, Inc.). Measurements were performed at resolution of 8.0 cm<sup>-1</sup> and 256 scans. The internal reflection element used for attenuated total reflectance (ATR) measurements was made by germanium with the entrance angle of 30°. Surface and cross section of the vulcanizates were observed by focused ion beam scanning electron microscopy, FIB-SEM (SMI-3050SE, Hitachi High-Tech Science Corp.) at accelerating voltage of 3 kV.

Phase measurement by dynamic mode and force-distance curve measurement using scanning probe microscopy (SPM) were carried out with MFP-3D-SA-J + SRC2 controller made by Asylum Technology Co., Ltd. A commercially available silicon tip on a rectangular cantilever with the bending spring constant of 1.08 N/m and with curvature of 7 nm (AC240TS-C3, Olympus Corp.) was used. The pull-off speed of the piezoelectric scanner for the measurements was 400 nm/s.

Composition of near surface region, ranging from surface to 10 μm in depth, of the CB filled IR vulcanizates was measured by thermogravimetry, TG (TGA/DSC1, Mettler Toledo Inc.). Samples of about 5 mg were heated in an alumina crucible by the following temperature program: 1) heating from 30 °C to 550 °C at a heating rate of 30 °C/min in N<sub>2</sub>, 2) combusting at 550 °C for 10 min in N<sub>2</sub>, 3) cooling from 550 °C to 300 °C at a cooling rate of 50 °C/min in N<sub>2</sub>, 4) annealing at 300 °C for 5 min in air, 5) heating from 300 °C to 650 °C at a heating rate of 20 °C/min in air and 6) combusting at 650 °C for 15 min in air, in this order. The amount of rubber, CB and ash were estimated from the weight loss of the CB filled IR vulcanizates on heating.

Molecular weight and molecular weight distribution of IR were measured by size exclusive chromatography (SEC). The sample used was pure gum unvulcanizate, since the vulcanizates were insoluble. The pure gum unvulcanizate of 200 μm thickness on a PET film was exposed with ozone at 20%RH and 80%RH for 120 h, respectively, and then, whole of the unvulcanizate was dissolved to tetrahydrofuran (THF) and filtrated. SEC measurements were carried out with a size exclusion chromatograph consisting of a differential refractometer detector (RI-101, Showa Denko K. K.), two tandem columns (Shodex GPC KF806 M, Showa Denko K. K.) and HPLC-pump (uf-3005SZB2, Uniflows Co., Ltd.). THF was used as an eluent at a flow rate of 1.0 mL/min. The Mark-Houwink parameters used were  $K = 1.76 \times 10^4$  and  $\alpha = 0.68$  for PS standard [20].

### 2.4. Ozone water treatment

Ozone water treatment of the CB filled IR vulcanizates was carried out with 250 ppm ozone at 23 °C for 2 h under non-stretching. Ozone was generated from dry and highly purified oxygen gas by using a laboratory ozone generator (LABO-ozone-250,

**Table 1**  
Compounding formulation.

Ingredients	CB filled compound	Pure gum compound
Isoprene rubber	100	100
Carbon black (IRB)	35	–
Zinc oxide	5	5
Stearic acid	2	2
Sulfur	2.25	2.25
Accelerator (TBBS)	0.7	0.7

Unit: phr

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