

Characterization of ozone-degraded composite of crosslinked polydimethylsiloxane with silica in water



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ABSTRACT

Effect of ozone-charged water on degradation of silicone rubber, i.e., crosslinked polydimethylsiloxane/silica composite, was investigated by various analytical techniques, in which active species including active oxygen were generated by self-decomposition of ozone in water. The composite was less swollen with good solvent after degradation with ozone-charged water, whereas amount of extracted polydimethylsiloxane increased significantly, reflecting chain scission of the polymer. Hardness of the composite, measured with scanning probe microscope and hardness tester, was found to increase after degradation. The extracts were proved to be polydimethylsiloxane through FT-IR and GC-MS. The composite was characterized through DD/MAS and CP/MAS solid state NMR spectroscopies on ¹³C and ²⁹Si nuclei. It was found that –O–Si(OH)(CH₃) groups were made in polydimethylsiloxane due to oxidative reaction with hydroxyl radical and they were attracted to silica in the composite to result in the decrease in the swelling ratio and the increase in the hardness.

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1. Introduction

It is of great importance to realize effects of ozone on polymers for medical and daily applications in water, since ozone is useful for various fields, i.e., disinfection of medical devices, deodorization of sanitary products, purification of water and so forth [1,2]. The reaction of ozone with the polymers in water may be distinguished from that in air, since ozone is known to generate active species including active oxygen in water as it undergoes self-decomposition [3–7]. Therefore, we have to carefully investigate the degradation of the polymers with ozone in water; that is, model reactions may be examined in ozone-charged water under various conditions, i.e., concentration of ozone in water, flow rate of ozone inlet, bubble size, agitation speed, temperature, pressure and so forth. Furthermore, attention may be also paid for its transient life time in nature and persistence in the reaction vessel without charging.

Silicone rubber, i.e., composite of crosslinked polydimethylsiloxane (PDMS) with silica, is well known to be superior in ozone resistance, oxidation resistance, thermal resistance,

radiation resistance and so forth. This may be explained to be due to extremely high bond energy of siloxane linkages in the main chain molecule [8], which results in a high chemical stability against ozone, heat, radiation and so on. Thus, the silicone rubber is able to be useful for heavy duty products: that is, roller for copying machine, cylinder head gaskets for engine, rubber hose for turbo-engine and O-ring for reactor pressure vessel of atomic power plant, which are utilized in air under severe circumstances such as high ozone concentration, high temperature and high level of radiation [9–11]. Furthermore, the silicone rubber is applicable to medical devices and sanitary products, which are used in water containing ozone. However, degradation of the silicone rubber and deterioration of silicon rubber-products with ozone in water have not been investigated, at all, which was distinguished from those in air. For example, no study on the reaction between PDMS and active oxygen in ozone-charged water has been performed, so far.

The active oxygen in ozone-charged water is widely recognized to be highly reactive with various organic substances including polymers. For instance, in the previous works, we investigated reactions of the active oxygen in ozone-charged water with ethylene-propylene-ethylidene norbornene terpolymer (EPDM) [12]. The degraded EPDM was found to possess hydroxyl, carbonyl and carboxyl groups along with the main chain molecule, when it was

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characterized by nuclear magnetic resonance (NMR) spectroscopy [13]. Furthermore, chain scission occurred during degradation, as is evident from decrease in the molecular weight measured by size exclusion chromatography (SEC). These may be concerned with the reaction of the active oxygen with EPDM. Ozone in water may react with hydroxyl anion to generate superoxide radical anions and hydroperoxyl radicals, which may produce various active species such as hydroxyl radical containing product during chain propagation reaction [3–7]. Particularly, hydroxyl radical is prominent as oxidant, which has the second highest oxidation-reduction potential (2.810 V {298 K}) following fluorine molecule, which has the first highest oxidation-reduction potential (3.076 V {298 K}) in nature [14]. These oxidation-reduction potentials are higher than that of O_3 (2.070 V {298 K}) [14]. The hydroxyl radicals ($k = 10^9\text{--}10^{10} \text{ M}^{-1}\text{s}^{-1}$) may rapidly react with saturated carbon hydrates, which may less react with O_3 ($k = 10^{-2} \text{ M}^{-1}\text{s}^{-1}$) [15,16]. The active oxygen may abstract hydrogen from EPDM, randomly, to form carbon radicals on the main chain molecule (polymer radicals). The resulting polymer radicals may react with hydroxyl radical to form hydroxyl group and with various active oxygen species to form carbonyl and carboxyl groups. Similar reactions with the hydroxyl radicals may take place on PDMS. In this case, we need to consider the probability that the resulting hydroxyl groups of PDMS may react with silanol groups existing many on surface of silica, which is dispersed in PDMS matrix.

The reaction of the active oxygen with PDMS may be investigated by NMR spectroscopy, since change in chemical environment of constituents of PDMS reacting with the active oxygen is reflected into value of chemical shifts. Furthermore, the reaction between the hydroxyl groups of PDMS and the silanol groups of silica may be detected by solid state NMR spectroscopy. In contrast, the chain scission may be analyzed by SEC and gas chromatography-mass spectroscopy (GC-MS), which directly assess the chain scission due to the detection of the change in molecular weight and indirectly assess the degradation of PDMS due to the detection of cyclosiloxanes, respectively. In the present study, the degradation of the silicone rubber as a composite of crosslinked PDMS with silica was investigated in ozone-charged water. The degraded silicone rubber was characterized by high power decoupling magic angle spinning (DD/MAS) NMR spectroscopy, SEC and GC-MS, as well as Thermo-gravity (TG) and swelling measurements. In addition, changes in structure and properties of the silicon rubber were also investigated by cross polarization magic angle spinning (CP/MAS) NMR spectroscopy, hardness measurement, scanning probe microscopy (SPM), respectively, in order to evaluate interaction of PDMS with silica during degradation.

2. Experimental

2.1. Samples

The silica-filled PDMS used in the present study was commercially available composite of PDMS containing a trace amount of methylvinylsiloxane units and silica (HTV type, KE-931-U, Shinetsu Chemical), in which HTV represents high temperature vulcanizable PDMS, comprised of PDMS, silica and small amounts of additives such as plasticizer [17]. The composite was mixed with 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane at room temperature for 10 min in an open-roll mill, and the mixture was, then, cured at 433 K under reduced pressure for 1 h, followed by post-curing at 503 K for 1 h to prepare the crosslinked PDMS/silica composite sheets with sizes of $20 \times 20 \times 1 \text{ mm}^3$. The sheets were extracted in hexane for 16 h by using Soxhlet apparatus, followed by drying under reduced pressure for 48 h at 303 K.

2.2. Ozone treatments

Fig. 1 shows a schematic illustration of the apparatus for sample treatments. Ozone was generated from highly purified dry oxygen gas by using a laboratory ozone generator (LABO-ozone-250, Keinan Denki) at a production rate of approximately 0.5 l/min. Water used was purified by the ion exchange and distillation methods. The temperature of the water with ozone gas was fixed at 293 K. The saturated concentration of ozone in the purified water, determined by an iodometric titration method, was $5.5 \pm 0.5 \text{ mg/l}$. The treated samples were thoroughly washed by purified water, followed by drying under reduced pressure for 24 h at 313 K.

2.3. Determination of insoluble weight fraction of the samples in good solvents

The samples with cellulose filter paper were extracted in solvent (hexane, or hexane/ethanol = 8/1 v/v %) for 16 h by Soxhlet method. After the extraction, the insoluble residue was dried in vacuum for 48 h at 303 K. The insoluble fraction of the samples was calculated from the weight difference between Soxhlet treated and untreated samples.

2.4. Determination of equilibrium swelling ratio (α_{eq})

The samples were immersed into good solvent (hexane, or hexane/ethanol = 8/1 v/v %) at 303 K, until equilibrium swelling was accomplished (equilibrium state). During the swelling process, the solvent was sometimes replaced by fresh one. The α_{eq} was calculated by Equation (1).

$$\alpha_{eq} = \frac{\text{sample weight at the equilibrium}}{\text{sample weight at the dry state}} \quad (1)$$

2.5. Characterization

TG analyses were carried out in N_2 (100 ml/min) atmosphere on a Mettler Toledo TGA/DSC1. About 5 mg of samples was heated in an alumina crucible from room temperature to 973 K at a heating rate of 2.5 K/min.

All NMR spectra were obtained by a JEOL JNM-ECX 400. Solution state 1H NMR measurements were carried out at frequency of 400 MHz for $CDCl_3$ solution of samples at 298 K. ^{29}Si DD and CP/MAS and ^{13}C DD/MAS measurements were made at 79.4 and

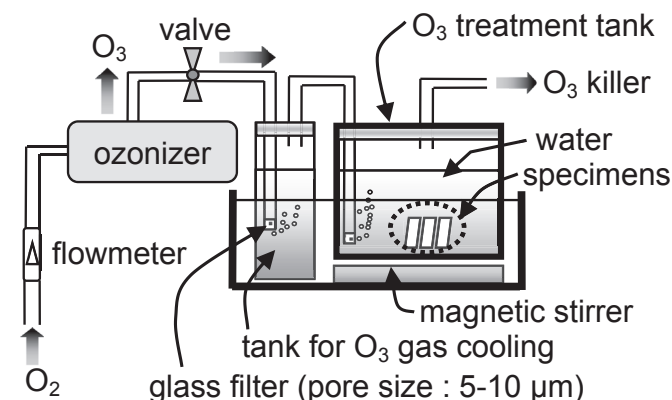


Fig. 1. Schematic representation of the home built apparatus for sample treatment.

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