Degradation of Poly(acrylic acid) in Aqueous Solution by Using O₃ Microbubble

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Polyacrylic acid (PAA) aqueous solution was treated with O₃ microbubbles and O₃ water, there was no difference in decrease in molecular weight of PAA due to the presence or absence of microbubbles. Regardless of dissolved O₃ concentration, O₃ microbubbles alone did not cause reduction in total organic carbon (TOC) and mineralization did not proceed. In the advanced oxidation process with hydrogen peroxide added, the molecular weight and TOC decreased. It is considered that active oxygen is generated from hydrogen peroxide by advanced oxidation and PAA is decomposed. From these results, it is no considered generation of reactive oxygen species by microbubbles in the decomposition of PAA.

Keywords: O₃, Microbubbles, Poly(acrylic acid), AOP, Polymer degradation

1. Introduction

Microbubbles are tiny bubbles with diameters of less than few tens micrometers and possess superior characteristics differing from those of normal bubbles with diameters exceeding millimeters. It has been reported that the rising speed is slow, that the pressure inside the bubbles is large, the gas dissolving ability is excellent, and the concentration of charges on the gas-liquid interface [1,2]. In addition, hydroxyl radical generates from decomposition of water by released energy of accumulated ions at the gas-liquid interface when microbubbles collapse in water [1]. The hydroxyl radical can degrade organic compounds with significantly strong oxidation power. For these reason, microbubbles have attracted much attention as an environmentally friendly cleaning technique in various fields such as medical treatment, agriculture, and water treatment [3,4].

As the internal gas of microbubbles, O₃ is often used. O₃ has a strong oxidation power and is applied to waste water treatment and semiconductor manufacturing [5-11]. O₃ water degrades compounds with C=C bond to carboxylic acid [12,13]. Additionally, O₃ generates reactive oxygen species through self-decomposition in water. Consequently, it anticipated that O₃ microbubbles effectively generate reactive oxygen species with two processes of the microbubble collapse in water and the self-decomposition of O₃ in microbubble-water interface (Fig.1).

![Fig. 1. Mechanism of hydroxyl radical generated from O₃ microbubble.](image_url)

We previously demonstrated the removal of photoresists and their base-polymers such as novolak resin, polyvinyl phenol and poly(methyl methacrylate) by using O₃ microbubbles [14,15]. The removal rate of novolak resin and polyvinyl phenol thin films increased by using O₃ microbubbles compared to O₃ dissolved water. The dissolved O₃ concentration increased, eventually promoting polymer degradation. O₃ microbubbles have a higher dissolved O₃ concentration than O₃.
water when the supply gas concentration is the same. On the other hands, a significant effect of microbubbles on degradation of novolak resin and polyvinyl phenol thin film could not be confirmed when the dissolved O\textsubscript{3} concentration was the same. Poly(methyl methacrylate), which has no C=C bond in the structure, could not be removed from Si wafer by O\textsubscript{3} microbubble. Reactive oxygen species are generally short lifetime, and no significant effect of microbubble on the film removal process confirmed in the previous study [16-21]. As further consideration, the degradation of polyethylene glycol (PEG) in aqueous solution by using O\textsubscript{3} microbubble was evaluated, and the effect of microbubbles was confirmed by decrease of the molecular weight and amount of total organic carbon (TOC) in PEG aqueous solution [22].

In this study, decomposition process after O\textsubscript{3} oxidation is examined by decomposing PAA having carboxylic acid in the side chain which is thought to be formed when side chain of polyvinyl phenol is decomposed by O\textsubscript{3}. It is aimed to verify whether backbone decomposition due to microbubble-derived active species has occurred.

2. Experimental

2.1. O\textsubscript{3} microbubbles generation systems

Figure 2 shows a schematic diagram of the O\textsubscript{3} microbubble generator. Microbubbles were generated using pressurized dissolution method. O\textsubscript{3} gas was dissolved by pressurizing with 0.4 MPa using a bellows pump (ΣP - 15 D - V, Sigma Technology Co.). An O\textsubscript{3} aqueous solution in a supersaturated state was generated and opened to the atmosphere through a dispersion nozzle (Resource Development Co., Ltd.) to generate a micro bubble.

Dissolved O\textsubscript{3} concentration was measured using the O\textsubscript{3} monitor (Ebara Kogyo Co., Ltd.). A low-pressure mercury lamp with an emission wavelength of 253.7 nm was used as the light source. O\textsubscript{2} water was supplied to the detection part, and the dissolved O\textsubscript{3} concentration was measured by measuring the ultraviolet absorption amount.

2.2. Decomposition treatment of PAA by O\textsubscript{3} microbubbles

O\textsubscript{3} microbubbles were generated in 3 L of ion exchanged water. Dissolved O\textsubscript{3} concentration was stabilized at 5 and 20 ppm at 21 ± 1 °C water temperature. 160 mg of polyacrylic acid (M\textsubscript{n} 25,000, Wako Pure Chemical Industries, Ltd.) was dissolved in O\textsubscript{3} microbubbles and O\textsubscript{3} water and stirred for 90 minutes. The molecular weight of PAA was measured using Gel Filtration Chromatography (GFC). GFC was measured by concentrating the sampled sample 20 times by distillation under reduced pressure. Total organic carbon (TOC) of PAA was measured using combustion catalyst oxidation method. O\textsubscript{3} microbubbles having a dissolved O\textsubscript{3} concentration of 20 ppm as an accelerated oxidation system and hydrogen peroxide 10 mM were added to O\textsubscript{3} water, and the PAA treatment was similarly carried out.

3. Results and discussion

3.1. PAA degradation by using O\textsubscript{2} microbubbles

Figure 3 shows the elution curve of the PAA aqueous solution subjected to oxygen microbubble treatment in order to examine the effect of crushing microbubbles. The dissolution curves in Figures 3b and c, which were treated with oxygen microbubbles for the untreated O\textsubscript{3} microbubble elution curves, remained unchanged. In oxygen microbubbles, decomposition of PAA did not occur. Therefore, it seems that active species such as hydroxyl radicals due to collapse of microbubbles are not generated (Fig. 1 top).
3.2. PAA degradation by using O3 microbubbles

Figure 4 shows the GFC elution curve of PAA treated with O3 microbubbles for 90 minutes at a dissolved O3 concentration of 5 ppm. Molecular weight of PAA treated with O3 microbubbles on O3 untreated elution curve decreased. The $M_n$ of PAA was about 6500. However, the molecular weight of PAA treated with O3 water having the same dissolved O3 concentration was almost the same as O3 microbubble treated. Figure 5 is an elution curve of PAA treated with O3 microbubbles and O3 water having a dissolved O3 concentration of 20 ppm. When treatment was carried out for 90 minutes, the $M_n$ of PAA decreased to about 2,800. Also there was no difference in decomposition between O3 microbubbles and O3 water. Decomposition of main chain of PAA by O3 progressed.

3.3. PAA degradation by using AOP of O3 microbubbles and H2O2

Figure 6 shows the elution curve of PAA treated by O3 microbubbles with 10 mM hydrogen peroxide. $M_n$ decreased to about 5000 at the time of 10 min treatment and about 1000 when treated for 90 min. When hydrogen peroxide was added, significant reduction in molecular weight was observed even in a short processing time. In addition, the decrease in the molecular weight did not change depending on the presence or absence of microbubbles. In microbubbles that used AOP in combination, the influence of hydroxyl radical formation due to decomposition of hydrogen peroxide was greater than generation of active species by collapse of microbubbles.

Figure 7 shows the time course of TOC of PAA aqueous solution treated with O3 microbubbles and O3 water. When treated at a dissolved O3 concentration of 20 ppm, no decrease in TOC occurred with only O3 microbubbles and O3 water. For O3 microbubbles and O3 water using accelerated oxidation, when Treatment was carried out for 90 minutes, TOC decreased to 60% with respect to the initial value. As a result, mineralization of PAA has progressed. However, there was no difference in the decrease in TOC depending on the presence or absence of microbubbles. Therefore, progress of mineralization by microbubble-derived active species did not occur.
4. Conclusion

In order to investigate the decomposition effect by microbubbles, the polyacrylic acid aqueous solution was treated with the same dissolved O3 concentration. When oxygen microbubbles were used, the molecular weight of PAA did not decrease and decomposition did not proceed. There was no formation of active species due to collapse of oxygen microbubbles. In decomposition by O3 microbubbles, the molecular weight decreased more when the dissolved O3 concentration was increased. However, there was no difference in decrease in molecular weight between O3 microbubbles and O3 water. From this fact, no effect was observed due to active species derived from microbubbles for degradation of PAA. In AOP with hydrogen peroxide, the molecular weight of PAA decreased more efficiently than O3 microbubbles and O3 water alone. Also, a decrease in TOC was observed, and mineralization progressed. However, decomposition promotion effect by micro bubbles was not observed.

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