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Mechanism of microwave heating through molecular orbital method and bubble size profiles

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Abstract

In this study, mechanism of microwave heating on water was investigated through a combination of the experimental and simulation works on bubble formation. Fine bubbles were firstly observed and confirmed at the temperature below the boiling temperature of water using a reactor equipped with DLS system. It was hypothesized that thermal non-equilibrium condition such as a hot spot was formed under microwave irradiation. Secondly, the initial stage potential of bubble nucleation (clathrate), which consists of water molecules, was calculated through a molecular orbital method. From the experimental and simulation results, it was found that high energy was generated by the bubble collapse, reconstruction of water molecule clathrate, and repetition of clathrate formation and collapsing cause higher heating efficiency of microwave. Thus, it can be deduced that microwave heating is greatly influenced by clathrate formation and the collapse.

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Keywords: Microwave; nano-bubble, molecular orbital method; Dynamic light scattering

1. Introduction

Microwave heating is an attractive technology for more effective and efficient processes of variety products and materials. Its successful applications in industrial processes for better manufacturing and characterizing materials have also been widely acknowledged [1-5]. Microwave heating offers many advantages due to its abilities to promote homogeneous temperature distribution, high heating efficiency and quick thermal response by dielectric heating. In

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our previous studies [6], formation of nano-bubbles in dispersion medium was observed during the irradiation, and the effects of the microwave power and maximum temperature on bubble size were observed. Takahashi et al. (2007) pointed out that nano-bubbles play important roles in chemical reactions. They reported that faster and better reactions are due to highly active nano-bubbles [7]. Nevertheless, studies on the quantitative estimations of nano-bubble formation under microwave irradiation are very scarce in the literature. Moreover, mechanism of these phenomena is still not well-understood.

This research focuses on the investigations of nano-bubbles formation and collapsing during microwave heating. Their mechanism then was explained via experimental and simulation studies. By clarifying the mechanism of microwave heating, it is expected that even though thermal effect and non-thermal effect cannot be easily identified and verified, efforts in further enhancing microwave special effects can be recommended [8, 9].

2. Method

2.1. Experimental

In this study, suspensions of two types of monodisperse particle, PSL (Polystyrene Latex, Duke Scientific Corp.) and magnetite particle, Fe_3O_4 (Micromod Corp.), with particle size of 100 nm were used. Heat generation from the PSL due to microwave irradiation can be assumed negligible because its microwave absorbance properties such as dielectric constant and dielectric dissipation factor are much smaller than of water [10, 11]. However, heat was produced around the Fe_3O_4 particle because it shows higher dielectric property.

Bubble sizes were measured in the microwave reactor equipped with a DSL system and detailed DLS calculation procedures were describe in our previous study [6]. The operating conditions of the experiments are listed in Table 1. Bubble sizes were measured before boiling temperatures (40 and 90 ^oC) while bulk temperature was monitored using optical fiber inserted from the top of the reactor.

Table 1. Experimental conditions.

Suspension density [particles/mL]	Microwave Power [W]	Maximum temperature [^oC]
1.8×10^9	30, 50, 70, 100	40, 90

2.2. Simulation

Nonlinear shape of water molecule and strong hydrogen bond between water molecules have been generally acknowledged. Therefore, clathrates of water molecule are normally formed due to the hydrogen bond as illustrated in Fig. 1. Clathrates consist of multiple heterocyclic and heterocyclic clusters of water molecules. The hydrogen-bonded aggregates are constantly forming and breaking up, and the clathrate heavily vibrates during microwave irradiation. It is believed that the clathrate formation plays an essential role as bubble nuclei during microwave heating. The potential of clathrate of water molecule was calculated using molecular orbital method. Gaussian software (Gaussian R 03W Ver. 6, Gaussian, Inc.) [12, 13] was employed to simulate the optimized clathrate structure of water due to its ability to provide comprehensive molecular information such as electron density, bond condition and energy [14, 15].

To explain the mechanism of microwave heating, the following procedures were conducted. The ground states of the optimum molecular structures of the clathrate and water molecule were first calculated. Energy of the collapsed clathrate was then estimated as the energy difference between discrete water molecules. In this analysis, the basis of the calculation is HF/6-31G(d) [16], and it was assumed that water molecules around the clathrate can be neglected to avoid excessive computational times.

Four different types of clathrates consisting of 20, 24, 28 and 36 water molecules as shown in Fig. 1, were prepared and two types of the collapsing process were calculated. The first to the fourth water molecules were moved toward the inside or the outside of the clathrate. The clathrate lost the balance of dipole moment and finally collapsed and then energy of disordered form of clathrate was calculated. Fig. 2 shows an example of a collapsed clathrate structures and Fig. 2 indicates the structure after three water molecules from the original clathrate were shifted to the outside.

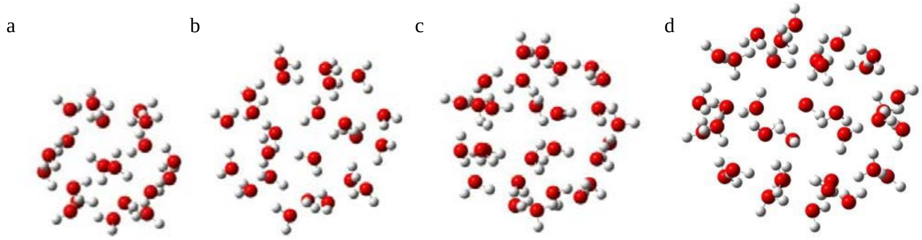

Fig. 1. Examples of clathrates structures of water molecules used in the simulations (a) 20; (b) 24; (c) 28; (d) 36.

Fig. 2. An example of molecular structures of a collapsed clathrate.

3. Results and discussion

3.1. Experiment

Fig. 3 shows examples of the profiles of bubble size and temperature in water during and after microwave irradiation. Filled and unfilled symbols indicate sizes during and after the treatment, respectively. Meanwhile, the red lines indicate the profiles of bulk temperatures. From these figures, it is obvious that bubble size increased as a function of time when the microwave is on. Temperature also increased and then gradually dropped after the microwave was turned off. It is also evident that generally the maximum bubble size was achieved before the microwave source was switched off. Fig. 4 presents the plots between maximum bubble sizes against irradiation power. From these figures (Figs. 4 (a) and 4 (b)), larger bubble size could be obtained at higher power and higher maximum temperature for magnetite particles. Moreover, bubble was formed below the boiling temperature even though the type of particle is plastic.

Generally, the hot spot exists at non-equilibrium conditions during microwave heating [17]. Internal evaporation around the hot spot is promoted by the rotations of polar molecules. Once the interface between liquid and air appears due to quick thermal response of microwave heating, the microwave absorbance energy is concentrated at the interface. Water molecules at the interface vibrate more actively because the bond at the interface becomes weaker than that of the bulk. Finally, after bubble nucleations, bubbles are rapidly growth. As a result, the energy is stored as fine bubbles. For magnetite particle, heat generation within the particle due to microwave absorption should be considered, and the bubble size is significantly influenced by the power. However, heat is released to the air from the wall of the container via convective heat transfer. At lower power, longer irradiation time is required than of the higher one to reach the designated temperature. Accordingly, when heat generation within the particle is negligible, bubble size became smaller at lower power.

Water molecule has natural molecular vibrations and forced vibrations under microwave treatment. However, there are distributions of electromagnetic field inside the liquid. Accordingly, some of the clathrates become larger bubble during the irradiation, and the others speedily become smaller. Theoretically, a temperature of 5000 K and a pressure of 100 MPa are generated within the nano-bubble [18]. This hot spot [17], which is created at the thermal non-equilibrium conditions, quickly spreads to the surrounding liquid. Energy stored as clathrates or fine bubbles is then released when they collapse. Consequently, repetitive process of bubble formation and collapse become important factors for microwave heating.

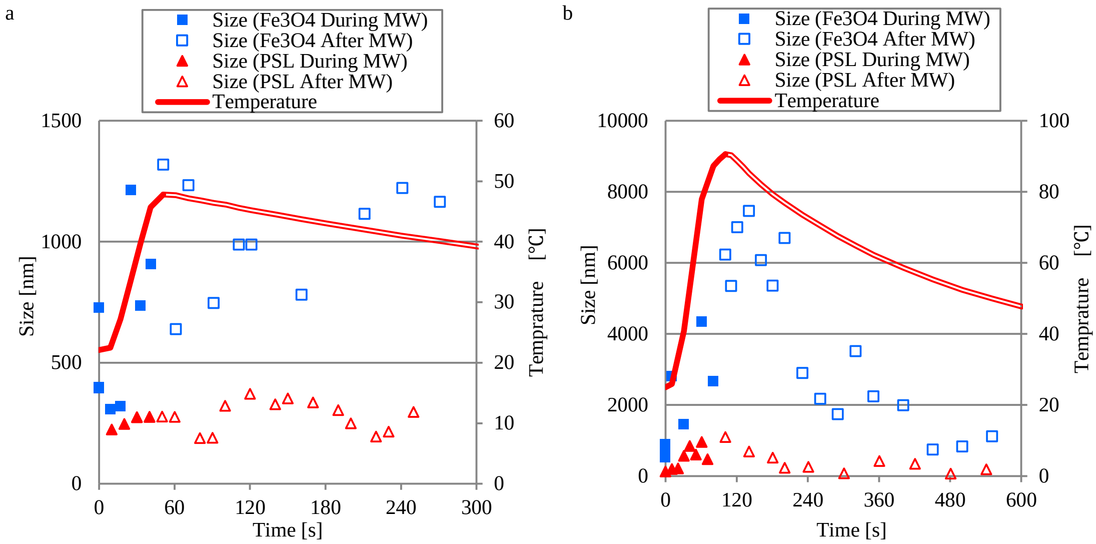

Fig. 3. Profiles of size and temperature during and after the irradiation at 70 W (a) 40 ºC; (b) 90 ºC.

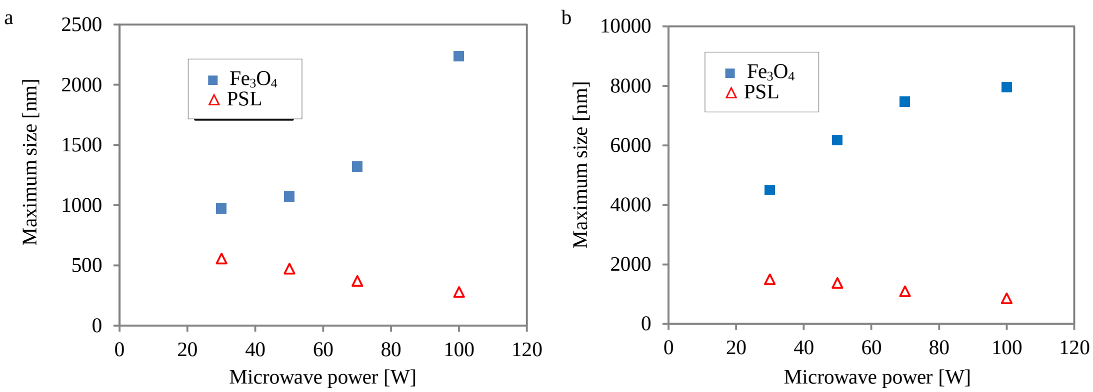

Fig. 4. Maximum size as a function of microwave power for the two dispersion mediums (a) 40 ºC; (b) 90 ºC.

3.2. Simulation

Energy released, when clathrate is collapsing, can be seen in Fig. 5. In this figure, energy was plotted against the number of water molecules. The asterisk marks indicate energy of the original clathrate. These data mean that the energy stored in a bubble is due to microwave energy absorbance. Water molecules constituting clathrate are strongly influenced and rotated by microwave irradiation because of their non-symmetry shapes and higher dipole moments. As a result, some of water molecules moved either outward or inward, and clathrate collapses. Filled marks represented the potential when water molecules moved. Clathrate then becomes more unstable as a consequence of further molecular rotations of continuous irradiation. Energy difference between the original and collapsed clathrates is released after the collapse. Some of hydrogen bond remains and the clathrate may not completely disappear. Incomplete clathrate becomes bubble nucleation again under continuous irradiation. The behavior of repetitive formation and collapsing is related to the quick thermal response of microwave heating due to high speed of the contraction [19]. When microwave irradiation causes continuous rotations of water molecules, the clathrate formation and collapse are repeated more frequently. Usually, microwave heating is explained using the phenomena of friction of the polar molecules [20]. Although clear observations of clathrates are difficult, the clathrates collapse releases higher energy and this indicates that it play an important role in the microwave heating.

Nano-bubble is generally active for chemical species decomposition because hydroxyl radical is produced by self-pressuring effect [21]. In this calculation, dispersion energy after the collapse is sufficient to decompose water molecule since the bond energy for H and OH is 499 kJ/mol [18, 19]. Thus, the formation of OH radical and unsteady behavior of this radical may be the influencing factors for non-thermal effect of chemical reaction. Under microwave irradiation, for example, by-product is negligible for radical reactions [22]. Energy release from nano-bubble formation and collapse during microwave, therefore, causes not only quick heating but also promotion of the chemical reaction. On the other hand, the clathrate escaped from the collapse, rapidly grows up during the irradiation and it was measured as nano-bubble by DLS as shown in Fig.3.

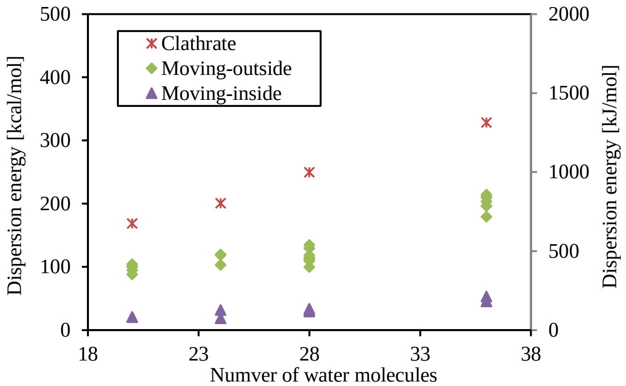

Fig. 5. Relation between energy and number of water molecules.

4. Conclusions

Bubble sizes were measured during and after microwave irradiation and mechanism of microwave heating was discussed. Bubble sizes rapidly increased during irradiation, and gradually became smaller after the irradiation was turned off. The maximum bubble sizes were strongly influenced by the type of particle, and bubbles were generated at below the boiling temperature due to the hot spot of thermal non-equilibrium condition of microwave irradiation. The profiles of the bubble sizes during and after irradiation can be explained by the bubbles growth, contraction due to temperature drop and the self-pressurizing effect of nano-bubbles. Moreover, energy of the original and collapsing clathrates was estimated using a molecular orbital method. It was found that high energy is released after the clathrates collapse. Therefore, apart from the friction of water molecule, based on the experimental data and molecular orbital method based simulation, behaviors for the formation and the collapse of clathrate were found to be influential in microwave heating.

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