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主 論 文 の 要 旨

論文題目　QUANTIFICATION AND INTENSIFICATION OF SONOCHEMICAL EFFECTS (ソノケミカル効果の定量的評価と強化に関する研究)

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論 文 内 容 の 要 旨

1. Background and purpose:

When ultrasound is irradiated into liquids, it first generates small bubbles; and then these bubbles collapse, and a local reaction field that makes the solution temperature and pressure able to alter enormously to 5000 K and 1000 atm, emerges. Consequently, distinct chemical and mechanical effects can be observed. Mechanical effects are caused by shock waves and micro-jet generated in irradiated solution. They cause the acceleration of mass transfer of solute and solvent. Under sonication, water molecule is decomposed, which creates highly reactive ·OH and ·H radicals. These radicals are the origin of chemical effects. Chemical and mechanical effects are defined as sonochemical effects. This study concentrated on quantification and intensification of sonochemical effects.

2. Mechanical effects quantification:

In order to advance the usage of ultrasound in industry, chemical effects of radicals have been studied and confirmed by many researchers. However, the dependence on frequency of mechanical effects is not clear yet. Hence, the aim of this research is to provide a simple, cost effective method to quantify mechanical effects and to clarify the frequency dependence of these effects. Mechanical effects were investigated through the viscosity change in degradation of polymers under sonication in aqueous and benzene solutions. Polyethylene oxide (PEO) with molecular weight of 900,000 and 100,000 was used with aqueous solution (abbreviated as PEO900 and PEO100W, respectively). *t*-BuOH was added in aqueous samples as radical scavenger to suppress the effects of radicals. Polystyrene with the molecular weight

350,000 and PEO with molecular weight 100,000 (abbreviated as PS350, and PEO100B, respectively) were studied in benzene solvent. Frequency range from 20 kHz to 1 MHz was investigated with various types of apparatus, under a constant dissipated power (5 ± 0.5 W). Viscosity ratio, η_{son}/η_{non}, where η_{son} and η_{non} are the viscosities of five min sonicated and non-sonicated samples, respectively, decreased remarkably for first five min of irradiation then the degradation slowed down. Mechanical effects were first evaluated by apparent degradation rate. Mechanical effects have frequency dependence in a tendency that the higher frequency is, the smaller the apparent degradation rates are in both aqueous and organic solutions. In other words, mechanical effects decrease as the frequency increases. However it is difficult to quantify mechanical effects using apparent degradation rate due to the complexity. In case of the analysis of solution viscosity, the viscosity ratio was evaluated (Figure 1). Viscosity ratio induced by horn at 20 kHz (with symbol ★ in Figure 1) is deviated from the others in PEO900. The connected line is viscosity ratio for NFLT50. This result shows the similar frequency dependence in both aqueous and benzene solutions to apparent degradation rate. From this consideration, measurement of viscosity ratio gives an alternative simple, cost effective method to quantify mechanical effects in sonochemistry.

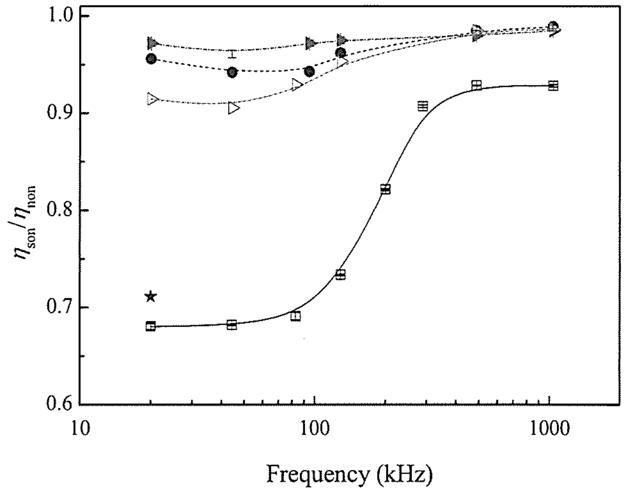

Figure 1. Viscosity ratios after five min irradiation of polymer in solutions at different frequencies at 5 ± 0.5 W. At 20 kHz, the data of degradation by horn (★) was not connected to the degradation tendency line at other frequency. □: PEO900 in aqueous solution with *t*-BuOH, ▷: PEO100W in aqueous solution with *t*-BuOH, ▶: PEO100B in benzene solution, and ●: PS350 in benzene solution.

3. Sonochemical reactor development:

In mechanical effects quantification study, the low efficiency of apparatus at 20 kHz between a horn and a new-built Langevin transducer was noticeable. Although low frequency of ultrasound, especially 20 kHz, has promising applications in industry due to its high intensity and mechanical effects, the unbalance in energy distribution or weak efficiency of sonochemical reactor prevents it from wide usage in industry. Moreover, at low frequencies, chemical effects are weak. The vibration plate of conventional Langevin transducers is fixed at the antinode of the transducer while the horn type transducer was fixed at its node. This

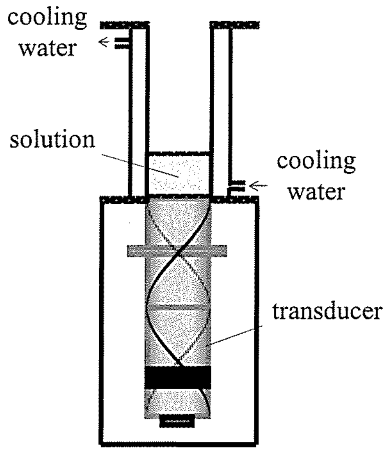

Figure 2. NFLT50 sonication apparatus.

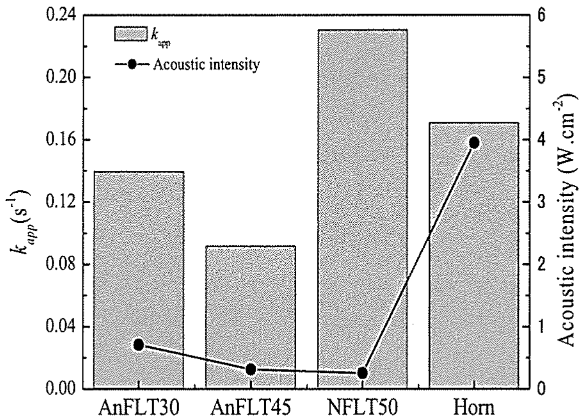

Figure 3. Degradation rate constant and acoustic intensity in PEO solution with *t*-BuOH upon sonication using different transducer types.

leads to the unstable oscillation of liquid in solution in the Langevin-type apparatus, which causes a decrease in degradation of polymer in solution in mechanical effects quantification. Therefore, a new transducer named NFLT50 was developed based on the structures of horn and Langevin transducer (Figure 2). Chemical and mechanical effects of two conventional Langevin transducers (named as ANFLT30 and AnFLT45), a horn, and the NFLT50 were obtained and compared. In Figure 3, the degradation rate constant for the NFLT50 transducer is the highest as compared to the others. With the improvement in structure, the NFLT50 showed remarkable sonochemical efficiency compared to those of other transducers (Figure 3). It is also the first time that standing wave was observed by sonochemical luminescence at this frequency. Standing wave formation was supposed to increase chemical effects. The reduction in observed wavelength was interpreted in terms of the coupled vibration mode.

4. Sonochemical effects intensification:

For intensification purpose, liquid height in the NFLT50 was changed from 30 to 200 mm to investigate sonochemical effects and the cavitation bubbles reactive zone. Chemical effects were evaluated with the *SE* value by the oxidation of I^- to I_3^- with the 0.1 M KI solution in a 15 min sonication. When liquid heights changed from 30 to 200 mm with the NFLT50, mechanical effects were suppressed as the liquid height increases. In case of chemical effects of the NFLT50, the *SE* values were similar to those of conventional ones with liquid height under 120 mm (Figure 4). However above this height, chemical effects induced by the NFLT50 transducer are improved remarkably. The improvement in the *SE* values is explained by the node-fixed structure of the transducer, which enables the formation of standing waves. Also in Figure 4, together with the increase of liquid height, the impedance changes in a repeat cycle with a decrease in amplitude. When resonance occurs in solution, the impedance is minimum, which accelerates the power delivered into solution. It is obvious that when the impedance is the lowest, chemical effects gain their highest.

When a standing wave is formed in luminol solution, bright zones reflect the most crowded zones of active and transient bubbles. Cavitation bubbles active zone visualization was carried out with sonochemical luminescence and aluminum foil destruction at a constant electric power of 40 W. As liquid height increases from 30 to 200 mm, bright zones increase in number from 1 to 8 (Partly plotted in Figure 5). At the same liquid height, the expected zones due to sonochemical luminescence were also observed in the aluminum foil destruction experiments with the correspondent positions. Standing waves are formed every half-wavelength, which is the distance between two nodes.

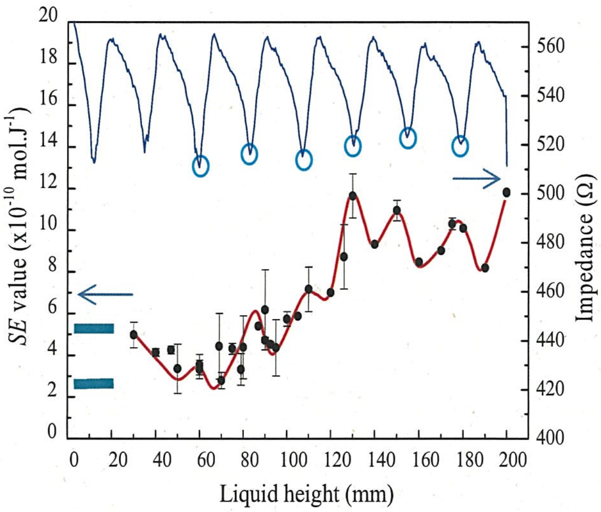

Figure 4. *SE* and impedance as functions of liquid height at 40 W of electronic power.

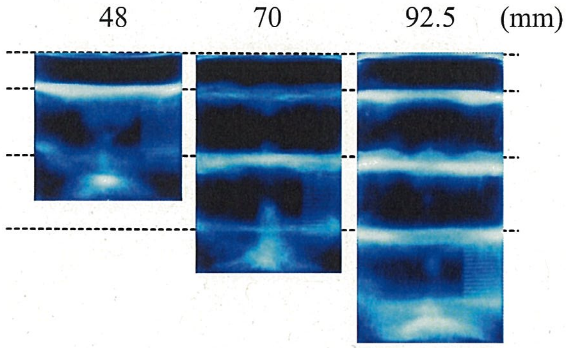

Figure 5. Standing wave formation as function of liquid heights at 40 W of electric power.

5. Conclusions:

Mechanical effects are suggested to be quantified by the degradation of polymer solution in solution. After five min of irradiation, the viscosity of solution is estimated, from which mechanical effects can be evaluated. This method using viscosity ratio is simple, cost effective and familiar to all chemists.

With the new transducer at 20 kHz, the NFLT50, the sonochemical effects are improved. Moreover, the stable vibration in the transducer is attributed to the formation of standing wave at this frequency.

Chemical effects are improved with increase of liquid height. And cavitation bubbles are found to reach their maximum activation at an optimal power.