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Study of Degradation of Polymer in Solution at 20 kHz Sonication

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1. Introduction

Recently, ultrasound is studied widely due to its enormous effects. Without initiator, its simple apparatus creates a tremendous high change in temparature and pressure during cavitation at room temperature. It has a promising application in industry. 20 kHz is a common frequency used in laboratory. As a high intensity ultrasound source, the effects of this frequency have been used for comparision with those of higher frequency. There are normally two types of transducer at this frequency: Horn or flat one (Langevin type). Although both transducers convert electrical energy to ultrasonic energy, the difference in the shape and area of them cause difference in degradation.[1] Both horn and Langevin type transducers give direct contact between solution and transducer. This leads to a high efficiency of transferring ultrasonic energy.

Besides, there are many researches on the sonoluminescene effects at this frequency; there are still lack of studies on mechanical and chemical effects in degradation of polymer 20 kHz. By using horn and Langevin type transducer, this research examined the difference of these effects by changing in dissipated power, sample volume and position of the horn.

2. Experiment

Polyethylene oxide (PEO) (SIGMA) with molecular weight 900,000 was dissolved into water at concentration 2 g/L. To investigate mechanical effects of ultrasound at 20 kHz, *t*-BuOH (guaranteed grade - Wako) was used as radical scavenger at 100mM to suppress the effects of chemical effects of radicals. Two types of transducer were used: Horn type (SONIFIER 450D, BRANSON) and directly irradiation type (a home-made apparatus with Langevin transducer from Honda Electronics Co. Ltd.) (**Fig. 1**). Diameters of transducers of direct type cell and horn type cell are 5.68 cm and 1.27 cm, respectively. The power delivered into solution was measured by calorimetry. Sonication was carried out at 20 °C. The temperature of samples was kept constant

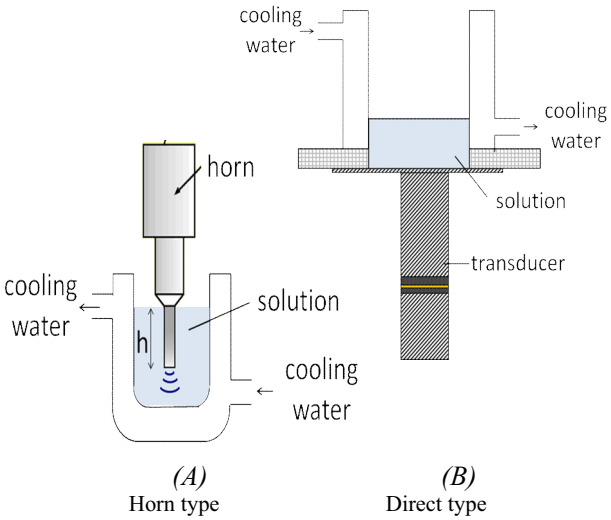

Fig. 1 Sonication apparatus

during irradiation by temperature controller. Degradation efficiency was evaluated by viscometry at 25 °C by Ubbelohde viscometer. Molecular weight was calculated from Mark-Houwink-Sakurada equation of PEO at 25 °C.[2]

Influence of depth of horn which is defined as the distance between the surface of the solution and the tip of the horn (as illustrated as *h* in Fig. 1A) was studied by changing the depth from 1.3 cm to 3.3 cm.

3. Results and discussion

For short time of irradiation, the degradation is assumed to be first order reaction as in below equation:

$$\ln\frac{M}{M_o} = -k_{app}t \qquad (1)$$

where M, M_0 are the molecular weight of sample at sonication time t and non sonicated sample, respectively. k_{app} is degradation rate constant. The degradation rate constant was calculated for the first five minutes of irradiation.

The degradation rate constants of PEO solution

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with *t*-BuOH of two transducers are presented in **Fig. 2**. Both experiments were carried out at 5 ± 0.5 W of dissipated power. Under mechanical effects of ultrasound, PEO in solution is degraded slightly stronger in horn type compared with Langevin type. The power which is delivered through area of horn's surface of horn type is about 20 times larger than that of Langevin one. However, as illustrated in Fig. 2, the differences in degradation rate constants are little. From this plot, it can be concluded that in comparing two sonochemical apparatus, the acoustic intensity is no need to be the same. The prerequisite condition is to keep the dissipated power constant.

There are many papers that studied the effect of horn height and reported the influence of solution height and horn height. In this research, the mechanical effects of horn at different height were studied. With the same volume of solution, the dissipated power measured at all height of horn is showed in **Fig. 3**. The power is 4.5 W, 4.6 W and 5.1W to 1.3 cm, 2.3 cm and 3.3 cm, respectively. This means that the power delivered into solution almost no change when the height of horn is change. This leads to the independence of dissipated power from horn height.

The degradation rate constant of *t*-BuOH presence samples, however, has the highest value at 1.3cm, which means the mechanical effects at 1.3 cm height have the strongest degradation results. This is attributed to reflection from the bottom of the cell and the solution flow in the cell.

In **Fig 4**, the height of the solution in the direct type cell was changed to study the wavelength effects at the same dissipated power (5W). Initial power intensity of direct type apparatus is 0.197 W/cm^2. The increase in the power density, which is defined by dissipated power per volume, leads to the increase in degradation of PEO in solution.

The difference between chemical and mechanical effects of ultrasound increases. For 20 kHz, the wavelength of ultrasound, λ, in water is 7.5 cm. As the solution level is higher than $\lambda/2$, in this case it is around 3.7 cm, standing wave appears. And due to the flow in the cell, the difference between chemical and mechanical effects may change as the height of liquid increases.

The efficiency of ultrasound depends on design of apparatus, the contact between solution and transducer, etc. The dependence of degradation of PEO in solution at 20 kHz in these parameters is still under investigated.

References

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2. A. Mehrdad, M.R. Rostami, Iranian Polymer Journal, 16 (2007) 795-801.

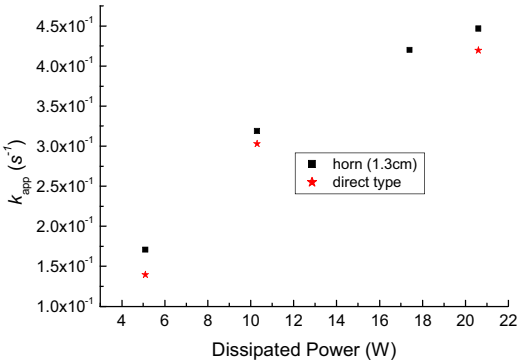

Fig. 2 Difference of degradation rate constant of PEO solution with *t*-BuOH between direct and horn type sonication. Explanation: cube (■): horn depth 1.3 cm; start (★): directly irradiation type

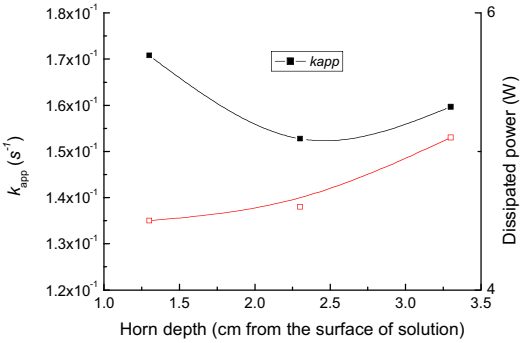

Fig. 3 Dissipated power and degradation rate constant at different horn height of PEO solution with *t*-BuOH in the horn type sonication. Explanation: cube (■): degradation rate constant; cube (□): dissipated power

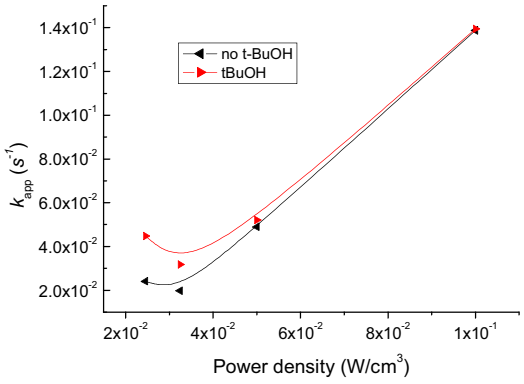

Fig. 4 Relation between degradation rate constant of PEO solution in direct irradiation type and power density at the same dissipated power (5W) condition. Explanation: triangle (◀): without *t*-BuOH; triangle (▶): with *t*-BuOH