Ultrasonic Resonance Scattering Analysis of Size-Controlled Particle Assemblies

Mayu Hiromoto[1‡] and Tomohisa Norisuye[1*] ([1]Grad. School of Sci. & Tech., Kyoto Institute of Technology)

1. Introduction

Ultrasonic analysis of microparticles dispersed in liquid has been performed using an ultrasonic scattering model of a simple sphere[1, 2]. On the other hand, the scattering behavior of an assembly of particles may be similar to that of sphere when an effective elastic modulus and density are considered. However, the scattering behavior of the particle assembly is not yet well understood, and at least the roles of inter-particle adhesion and connectivity were unclear. Supraball (SB) could be a promising material for electrochemical applications and optical materials owing to the large surface area and the internal packing structures[3] and could be employed as a model material to study propagation of ultrasound. Therefore, in this study, we investigate the propagation of ultrasound and the elasticity of SBs by the ultrasonic spectroscopy method.

2. Experiments

2.1. Preparation of SB

SBs were prepared by the so-called drying-in-liquid method as follows. The primary particle of SB is cross-linked polymethyl methacrylate (PMMA) particles purchased from Sekisui Chemical with nominal diameters of d = 300 nm, 500 nm, 1.64 μm, and 18.5 μm. These SBs are hereafter abbreviated as SB3, SB5, SB16, and SB190. Primary particles were uniformly dispersed in dichloromethane (DCM) or toluene, good solvent of PMMA to prepare a stock solution of suspension of oil phase. The droplets were made by the SPG emulsification method to make the SB3, SB5 and SB16. The water phase contains 1wt% sodium dodecyl sulfate, SDS as a surfactant to stabilize the DCM emulsion. In the case of toluene emulsion, we use 0.2wt% SDS and 1wt% F108 as a polymer dispersant. For SB190, preparation of monodisperse droplet using the SPG method was not allowed. Therefore, the oil phase was directly dispersed in water phase to make emulsion. Those emulsions were evaporated at 20, 40 and 60°C in a water bath with stirring at 350 rpm. After evaporation of solvent, the SBs were fractionated using two types of Merck nylon net filters with nominal pore diameters of 20 and 41 μm. SBs with diameters about D = 35 μm were thus obtained.

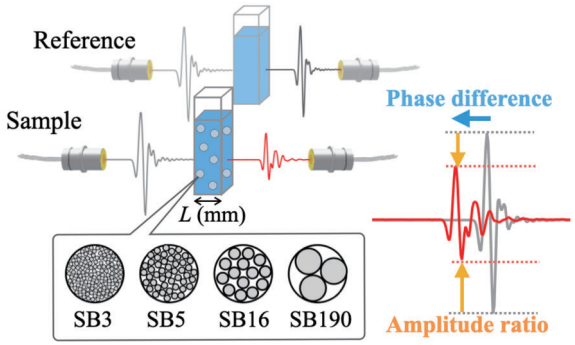

Fig. 1 Schematic of US measurements.

2.2. Ultrasonic spectroscopy (US) measurements

Fig. 1 shows the schematic of US measurements. The 20 MHz-longitudinal wave transducers manufactured by KGK were placed facing each other in water controlled at 25.000 ± 0.005°C, and the sample injected in a disposal polystyrene cell was placed between the transducers. A remote pulser BLP-12R, manufactured by iSL was used as a spike pulser. The transmitted pulse was received by a 12-bit high-speed digitizer, CS12400 GaGe Applied inc., with the sampling rate 200 megasamples per sec.

3. Results

First, primary particle size dependence of properties of SB swollen by DCM was investigated. All the SBs were evaporated in a water bath controlled at 20°C. When the attenuation spectra of the particle suspension were observed, a peak is observed at a frequency, indicating that the particle exhibited a solid resonance behavior since the wavelength of ultrasound is comparable with the size of particle. Similar behavior could be obtained for SBs if the packing of the particle is sufficient. Hereafter, the peak frequency is abbreviated as f_{MAX}. The peak frequency is also known to associated with an interfering wave surrounding the particle, where the velocity of surface wave c_R is related to the product of f_{MAX} and the particle diameter D through the relation $c_R = f_{MAX}D\pi/2$. In this study, D is obtained by an optical microscope. Since c_R is close to c_S, $f_{MAX}D$ could be a measure of particle rigidity (or packing density) through $G' = \rho c_S^2$. The packing density of the samples was also directly measured using the Z-DSS method[4].

Fig. 2 shows the primary particle size d dependence of $f_{MAX}D$ (left, black) and packing density φ (right, blue) of SBs prepared using DCM. While the $f_{MAX}D$ and φ of SB16 and SB190 are large, those of SB3 and SB5 were small. In order to prepare SB3 and SB5 with the larger packing density, we try to fabricate them in toluene at different temperatures.

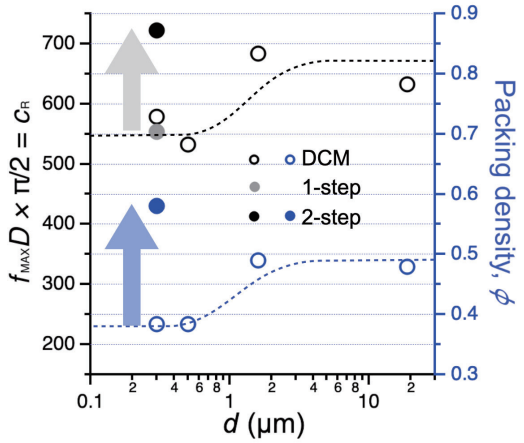

Fig. 2 Primary particle size dependence of surface wave velocity c_R and packing density φ of SBs.

SB3s prepared at different drying temperature 20, 40, and 60°C were investigated by US. In Fig. 2, the gray solid circle shows the $f_{MAX}D$ of SB3 prepared at 60°C. While the $f_{MAX}D$ increased with the preparation temperature, it was still lower than those of SB16 and SB190.

Fig. 3(a) shows the attenuation coefficient and phase velocity obtained for SB3 prepared at 60°C in toluene where the solid line indicates the theoretical calculation based on the ECAH single spherical scattering theory with c_{L2} = 2.3 (mm/μs), c_{S2} = 0.51 (mm/μs), ρ_2 = 1.07 (g/cm^3), C = 0.37wt%. Since SB3 is not a homogeneous spherical particle, the solid line does not match the experimental data.

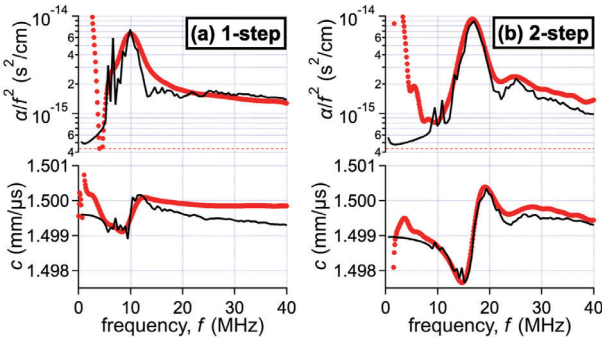

Fig. 3 Spectra of (a)1-step and (b)2-step method SB obtained by Ultrasonic spectroscopy.

During the fabrication process of SBs, we noticed that the reproducibility of $f_{MAX}D$ and φ was poor sometimes. The PMMA particles were swollen in solvent, followed by preparing SB after evaporation of solvent. In order to repeat this experiment, we have disassembled SB to collect the PMMA particle and prepare the sample again. Then we noticed that the packing of SB in the second time was better than that of the first time. Hereafter, importance of the 2-step fabrication method is addressed. An example of the US spectra of SB prepared at 60°C is shown in Fig. 3(b). The solid line indicates the theoretical curve obtained for a single homogeneous particle with the parameter c_{L2} = 2.1 (mm/μs), c_{S2} = 0.8 (mm/μs), ρ_2 = 1.107 (g/cm^3), C = 0.3wt%. The $f_{MAX}D$ and φ of SB3 is larger than that prepared by the 1-step method.

In Fig. 2, it is seen that $f_{MAX}D$ and φ obtained for the SB3 prepared by the 2-step method at 60°C was much larger than those by the 1-step method, and even larger than any other SBs including SB16 and SB190. We believe that this is due to polymer dispersant remained at the surface of the primary particles and rather penetrated into the primary particle at the first stage of preparation. A similar phenomenon was reported in literature[5]. By comparing two spectra in Fig. 3, one can realize that the acoustical spectra obtained for the 2-step method is now very close to spherical particle with homogeneous density, suggesting the obtained SB is fairly dense as studied by $f_{MAX}D$ and φ.

4. Conclusions

It was confirmed that the SBs prepared at the higher temperatures resulted in the higher packing density. The two-step method (recycling of particles) could produce higher packing density of SBs. It was found that the scattering of ultrasonic waves can be expressed by the scattering function of equivalent sphere with the effective properties as the packing density increases.

References

1) R.S. Al-Lashi and R.E. Challis. J. Acoust. Soc. Am. **138**, 1023 (2015).
2) K. Tsuji, H. Nakanishi and T. Norisuye. Ultrasonics. **115**, 106463 (2021).
3) G. R. Yi, V. N. Manoharan, S. Klein, K. R. Brzezinska, D. J. Pine, F. F. Lange and S. M. Yang. Adv. Mater. **14**, 1137 (2002).
4) T. Konno, T. Norisuye, K. Sugita, H. Nakanishi and Q. Tran-Cong-Miyata. Ultrasonics. **65**, 59 (2016).
5) A. J. Kim, V. N. Manoharan and J. C. Crocker. J. Am. Chem. Soc. **127**, 1592 (2005).

E-mail: ‡d1871002@edu.kit.ac.jp, *nori@kit.jp