Ultrasonic Scattering Analysis of Colloidal Particle Assemblies Composed of Particles of Different Elastic Modulus

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

1. Introduction

Supraball (SB) are size-controlled spherical particle assemblies consisting of primary nano- or micro-particles with a typical size ranging from a few hundred nm to several tens of μm. In recent studies, SBs have been investigated for applications that utilize the unique functionalities of nanoparticles. Such materials could be employed as a model.[1)]

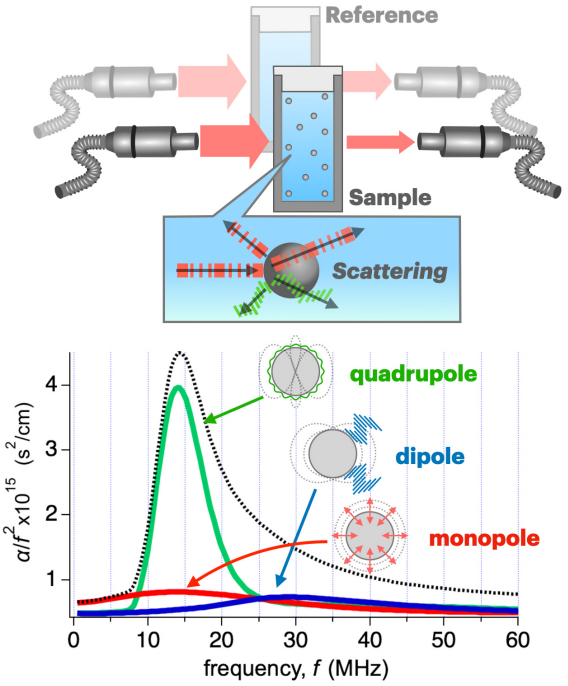

Fig. 1 Schematic of US measurements.

The ultrasonic spectroscopy (US) method is a technique to evaluate the physical properties of a sample based on changes in the amplitude and phase of ultrasonic waves transmitted through the sample. **Fig. 1** shows the schematic of US measurements. For example, the frequency spectrum of the ultrasonic attenuation coefficient through US measurement shows a peak, which can be related to the velocity of surface wave c_R surrounding the particle. Since c_R has been reported to be close to the shear velocity, c_R can also be converted to the shear modulus G'. The elasticity of particle assemblies seems to increase with the modulus of the primary particles. However, considering the inter-particle connectivity, small contacts between rigid particles may not be sufficient to support the high modulus of elasticity, because of the inefficiency of transmitting deformation. Therefore, in this study we prepared SBs of different compositions with two types of particles with different elastic modulus, silica particles and cross-linked polymethyl methacrylate (PMMA) particles, and systematically investigated the PMMA composition dependence of the surface wave velocity by ultrasonic spectroscopy.

2. Experimental Section

2.1. Preparation of SB

SBs were prepared from S/O/W emulsions fabricated by SPG membrane emulsification, using the liquid drying method, as follows (**Fig. 2**).

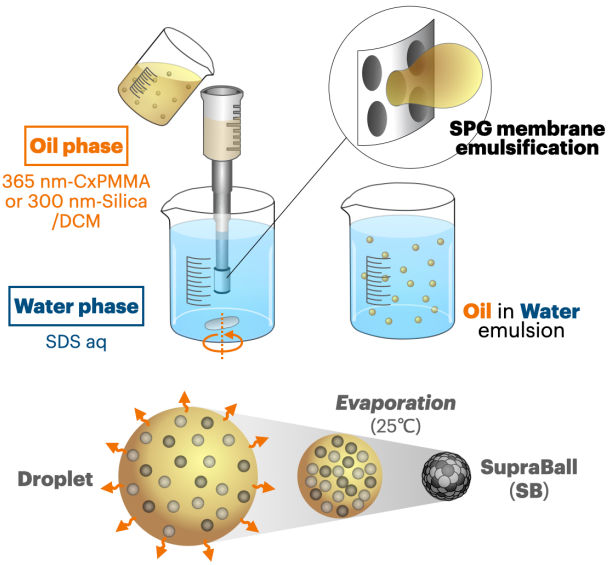

Fig. 2 Schematic of the binary particle assemblies formation process by the SPG method.

The primary particles of SB are cross-linked PMMA particles with nominal diameter of 365 nm purchased from Sekisui Chemical and silica particles with nominal diameter of 300 nm purchased from Nippon Shokubai. Silica particles were chemically modified by silane coupling agent, methoxytrimethylsilane, purchased from BLD pharm. The primary particles were mixed in various compositions and uniformly dispersed in dichloromethane (DCM), a good solvent, to prepare a stock solution of suspension of oil phase. Those emulsions were evaporated at 25°C in a water bath with stirring at 300 rpm to obtain SBs diameters of about 30 μm.

E-mail: ‡m3672014@edu.kit.ac.jp, *nori@kit.jp

2.2. Ultrasonic spectroscopy (US) measurements

US measurements were conducted in water controlled at 25 ± 0.005 °C. A sample in a disposable plastic cell of approximately 1 mm thick, dimension 10 x 10 x 40 mm^3 , was placed in the middle of two longitudinal plane wave transducers (KGK). The frequency f dependence of the attenuation coefficient α and phase velocity c were calculated by comparing the waveforms transmitted through the sample with those transmitted through the reference.

3. Results

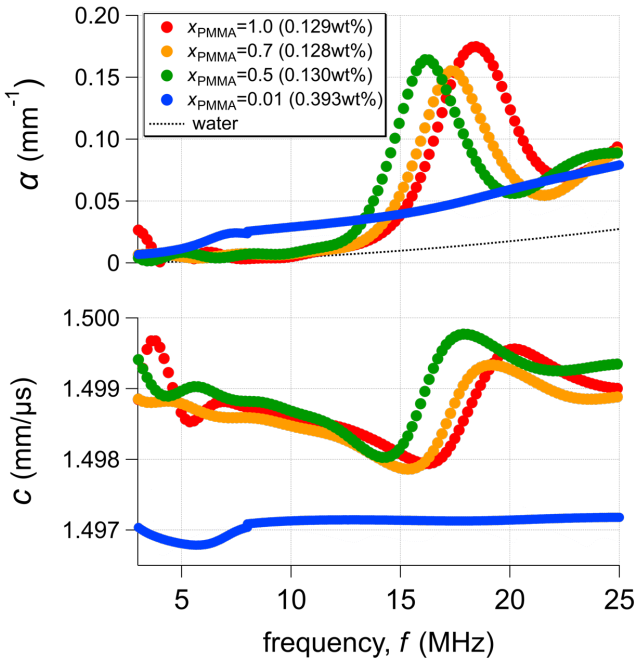

Fig. 3 The frequency spectra of α and c for different compositions of PMMA.

Fig. 3 shows the frequency spectra of α and c for different composition of PMMA. For the SB with PMMA : silica = 1 : 0 (x_{PMMA}=1), shown in red in the figure, the frequency spectrum of α have a peak at 18.5 MHz, while the peak shifted to lower frequencies with the decreasing PMMA composition. Finally, for the SB with PMMA : silica = 1 : 99 (x_{PMMA}=0.01), shown in blue in the figure, the peak shifted to 7.0 MHz. When approaching x_{PMMA} = 0, the shape of the peak became broad and it was difficult to determine the presence of the peak, but by measuring at higher sample concentrations, the peak could be found at SBs up to x_{PMMA} = 0.01. It is known that the velocity of surface wave c_R can be determined as $c_R = f_{max}d \times (\pi/2)$, using the peak frequency f_{max} at which the frequency spectrum of α reaches its maximum value and the diameter d of the particle.[2] Through this relation, c_R was calculated from f_{max} obtained by the US measurement and d obtained by an optical microscopy.

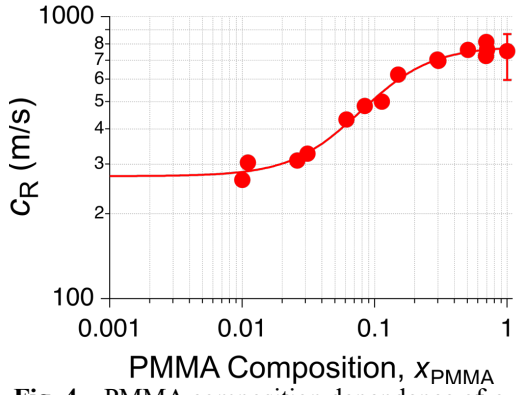

Fig. 4 PMMA composition dependence of c_R.

Fig. 4 shows x_{PMMA} dependence of surface wave velocity c_R. As a result, c_R increased with x_{PMMA} sigmoidally. As a primary particle, PMMA is softer than silica, but the experimental results show that the larger the value of x_{PMMA}, the larger the value of c_R. Our previous studies have proposed that PMMA particles are easily swollen in solvent, resulting in many contact points between particles and thus a high efficiency of elastic wave propagation. On the other hand, since silica particles are not swollen significantly in solvent, they behave as rigid primary particles. As a consequence, comparing silica and PMMA particles, it is possible that silica particles themselves are rigid, but the assemblies are fragile. The experimental results in **Fig. 4** were fitted using the following Hill function equation:

$$f_{max} = c_{R,Silica} + (c_{R,PMMA} - c_{R,Silica}) / \left\{1 + \left[\frac{x_{PMMA}half}{x_{PMMA}}\right]^{rate}\right\}$$

where $x_{PMMA}half$ is the PMMA composition at which the surface wave velocity reaches 50% of its maximum value. For x_{PMMA}= 0, c_R=272 is predicted by the fitting analysis, this corresponds to f_{max} = 5.8 MHz for SB with a particle size of 30 μm. Unfortunately, no significant peaks were observed in the spectrum of SBs in the frequency range, even at higher sample concentrations.

4. Conclusions

Using the US method, we systematically compared the rigidity of particle assemblies composed of two types of primary particles with different elastic moduli : silica and PMMA particles. The experimental results suggest that the overall rigidity of the particle assemblies is determined by the inter-particle connectivity rather than the rigidity of the primary particles themselves.

References

1) M. Hiromoto and T. Norisuye, Proc. 44th Symp. Ultrasonic Electronics, 2023, 3P1-3.
2) K. Ishimoto, K. Tsuji, M. Hiromoto, V. Leroy and T. Norisuye, Jpn. J. Appl. Phys. **63**, 02SP84 (2024).