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Ultrasonic Resonance Scattering Analysis of Colloidal Assemblies in Suspension

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1. Introduction

When an ultrasound pulse transmitting through a suspension of microparticles dispersed in liquid is measured by the ultrasonic spectroscopy (US) method with two ultrasonic transducers facing each other, the reduction of the wave amplitude compared to a reference liquid could be observed. This is due to scattering attenuation in addition to the viscus loss of the particles and liquid, and has been utilized to determine the size distribution and elastic moduli of particles in emulsions and suspensions. Fourier transformation of the transmitted waveform yields the frequency dependences of the transmitted amplitude and phase. By comparing these properties obtained for the sample and the reference, the ultrasonic attenuation coefficient α and phase velocity c can be obtained as a frequency spectrum. These can be analyzed using ultrasonic scattering theory, such as the ECAH theory proposed by Epstein, Carhart, Allegra and Hawley, to perform quantitative evaluation of particle size and elastic modulus[1]. Recently, we have applied the ECAH theory to viscoelastic microparticles and demonstrated the validity to the microparticles that possess both the viscous and elastic part of elastic moduli[2]. Ultrasonic scattering analysis has been frequently utilized for spherical particles of uniform density. However, quantitative studies of spherical particle assemblies (supraballs, which are aggregates with a well-defined structure) have been less common. This could be a promising material for electrochemical applications and optical materials owing to the large surface area and the internal packing structures[3]. In this study, we studied acoustic properties of supraballs made of monodisperse submicron-sized particles. Cross-linked polymethyl methacrylate (PMMA) particle was employed as the primary particles and the relationship between primary particle size and ultrasonic scattering properties of supraball were investigated.

2. Experiments

Supraballs were prepared by so-called the drying-in-liquid method as follows. 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 were uniformly dispersed in dichloromethane (DCM), good solvent of PMMA to prepare a stock solution of PMMA/DCM at 1wt%. Then, droplets of the PMMA/DCM solution were injected into distilled water by the SPG emulsification method, followed by DCM evaporation to have supraballs. The supraballs of PMMA particle with different d including a spherical PMMA particle with a constant density were schematically illustrated in **Fig. 1**.

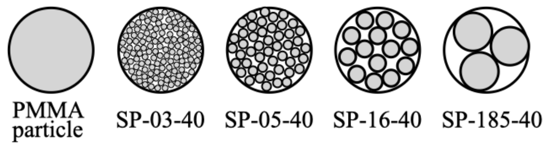

Fig. 1 Schematic representation of supraballs of crosslinked PMMA particles with different primary diameters d.

The emulsions were aged for 30 minutes at room temperature with stirring at 350 rpm. Two types of Merck nylon net filters with nominal pore diameters of 30 and 41 µm were used for fractionation of particles. Supraballs with diameters of D = 40 µm were obtained by filtration using these two types of filters. In this way, four types of supraballs were obtained. These four types of supraball are hereafter abbreviated as SP-03-40, SP-05-40, SP-16-40, and SP-185-40, respectively. Here, the preceding numbers are the diameters d of the primary particles used and the trailing numbers are the diameters D of the resulting supraballs.

The 20 MHz-longitudinal wave transducers manufacture by KGK were placed facing each other in water, and the sample was placed between the transducers. Excitation pulse of –330 V was generated by a spike pulser DPR500, JSR inc., equipped with a remote pulser H4, followed by transferred the pulse to the transmitting transducer. The generated ultrasonic waves transmit through the sample and are received by the transducers placed on opposite sides. By analyzing the signal received by a 12-bit high-speed digitizer, CS12400 GaGe Applied inc., with the sampling rate 200 megasamples/sec, a frequency spectrum of the attenuation coefficient α of ultrasonic waves transmitting through the particles suspension is obtained. The obtained spectrum was theoretically reproduced to analyze the physical properties and structure of the supraballs.

3. Results

Before discussing the frequency f dependence of ultrasonic attenuation coefficient and phase velocity of the supraballs, the calculated values of ECAH theory for uniform spheres were obtained as a function of frequency. **Fig. 2** shows the frequency dependence of α for PMMA particles of 40 µm diameter at the volume fraction ϕ = 1%. Although ultrasonic scattering can be described by the sum of various modes from $n = 0$ to ∞, in this particle size and measurement frequency range, the main contributions come from $n = 0$, which originates from compressibility difference between the particle and liquid, $n = 1$ from density differences, and $n = 2$, which represents quadrupole resonance. In particular, the contribution of $n = 2$ is found to be very large.

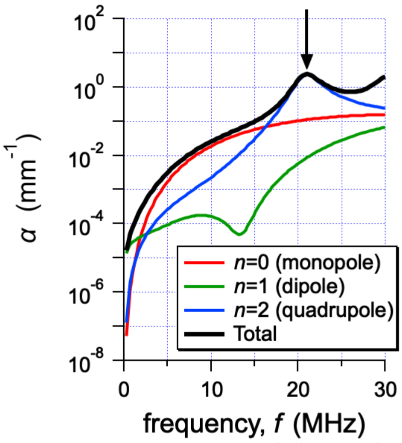

Fig. 2 Frequency spectra of the α obtained for the homogeneous spherical PMMA particles with diameters of 40 µm at ϕ=1%.

Fig. 3 shows α/f^2 of the supraballs with different ds. At around 10 MHz, noticeable peak was observed. In contrast to the case of simple spherical particle with a homogenous density demonstrated in Fig. 2, the locations of peak frequency of supraballs were found to be fairly low (21 → 10 MHz). Since the supraball is an assembly of PMMA particles filled with water in suspension, the longitudinal and shear velocities of supraball are expected to be smaller than the corresponding velocities of the PMMA uniform sphere. The solid lines in Fig. 3 are curves calculated to reproduce the experimental results with supraball's longitudinal and shear velocities, and density as adjustable parameters. While the longitudinal velocity of the supraball is considered to be determined by the composition of PMMA and water, the shear velocity can be zero or very small unless the PMMA transmits shear deformation inside the assembly. From this analysis, the shear velocities of supraball were determined to be 648 m/s, 615 m/s, 770 m/s and 740 m/s for SP-03-40, SP-05-40, SP-16-40, and SP-185-40, respectively. Among them, SP-16-40 exhibited higher resonance frequency,

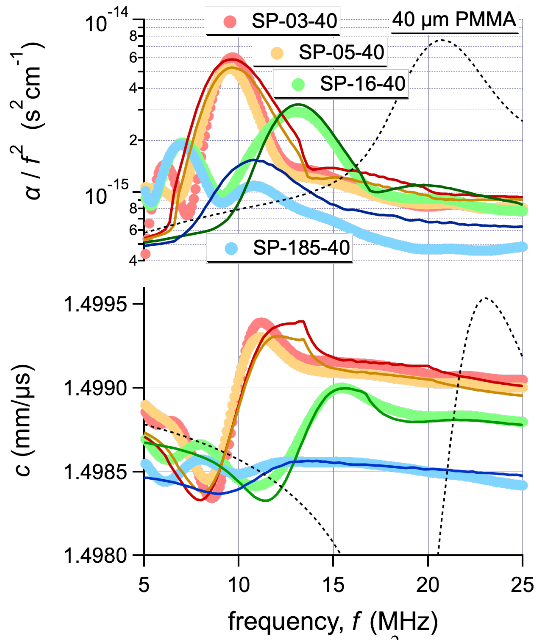

Fig. 3 Frequency spectra of α/f^2 and c obtained for the supraballs with different ds.

suggesting that the packing density is the highest among all the supraballs investigated in this study. In the presentation, the relationship between the structures and ultrasonic properties of the supraballs will be presented in detail.

4. Conclusions

Particle-assemblies called supraball were prepared by swelling crosslinked PMMA particles with dichloromethane and drying the solvent. An attenuation peak was found at a much lower frequency than that expected from a homogeneous particle, which may be attributed to the quadrupole resonance of the supraball. This means that the supraball has a relatively low shear modulus but propagates the shear deformation at the interface of primary particles inside the particle aggregate. In the future, we plan to measure the sedimentation velocity of the particles using dynamic ultrasound scattering method and investigate the correlation between the internal structure and ultrasonic properties of the assembly from the effective density calculated from the sedimentation velocity.

References

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