Ultrasonics xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Ultrasonics

journal homepage: www.elsevier.com/locate/ultras

Sound velocity and attenuation coefficient of hard and hollow microparticle suspensions observed by ultrasound spectroscopy

Kohjiro Kubo, Tomohisa Norisuye *, Thao Nguyen Tran, Daisuke Shibata, Hideyuki Nakanishi, Qui Tran-Cong-Miyata

Department of Macromolecular Science and Engineering, Graduate School of Science & Technology, Kyoto Institute of Technology Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

ARTICLE INFO

Article history:
Received 21 April 2015
Received in revised form 20 May 2015
Accepted 20 May 2015
Available online xxxx

Keywords:
Attenuation
Sound velocity
Scattering
Hollow particle

ABSTRACT

Size and elastic properties of micro-particles suspended in liquid can be acoustically determined by ultrasound attenuation and velocity measurements with the aid of elastic scattering theories and a dispersion relation. While quantitative evaluation for hard micron-sized spheres using the theories is available in literature, that for hollow particles is not yet achieved. In this study, we show that the shell thickness and the elastic modulus of hollow particles can be quantitatively evaluated by ultrasound spectroscopy. Several kinds of microparticles including polystyrene rigid particles, polydivinylbenzene rigid particles, borosilicate hollow particles, and phenolic-resin hollow particles were examined as a function of the particle concentration.

1. Introduction

Microcapsules or hollow microparticles have been an attracted research subject in many application fields, such as medical, aromatic, cosmetics, agricultural products and display, thanks to its unique microstructure and/or to encapsulation of functional molecules [1–3]. In order to monitor the stability of particle or the controlled release characteristics of the molecules from the microcapsule, it is crucial to evaluate the shell thickness and mechanical properties of the hollow microparticles. Among the wide variety of particle-sizing techniques, scanning electron microscopy is a popular and useful method. However, it generally requires pretreatment of sample prior to observation, such as drying of particles and a vapor deposition of gold in order to enhance the contrast for imaging. Needless to say, if the particles are fragile, the evaluated particle size and the structures no longer remain in its original form. On the other hand, static/dynamic light scattering [4], laser Doppler methods and other optical microscopy methods are promising techniques to observe the particle suspension as is. However, they have some difficulties to be used in optically opaque systems, such as concentrated solutions, suspensions containing micron-sized particles or aggregates accompanying strong multiple scattering of light. Therefore, in order to perform *in-situ* investigation of particle size and structures, an alternative approach may be required. The size and interactions of particles in a highly turbid suspension can be evaluated by novel ultrasound techniques based on dynamic scattering approaches [5–9], and more recently, the detectable particle size is extended down to 100 nm [10]. However, none of these techniques enables us to obtain the mechanical information of the shell part of microcapsule, which is very important to understand the stability of particle for practical applications, such as drug release.

Ultrasound spectroscopy is a non-contacting and non-destructive method, enabling us to monitor the acoustic properties of materials over a wide range of frequency [11–14]. In this study, we employ 20 and 30 MHz longitudinal ultrasound transducers whose wavelength is almost equivalent to the size of microspheres. At the intermediate regime of wavelength, the frequency dependence of the attenuation coefficient and the sound velocity is strongly affected by the presence of micro-particles, which involve the so-called resonance scattering. Faran proposed an acoustic scattering theory [15] for an elastic rigid particle with the radius a immersed in an inviscid liquid by solving three boundary conditions for the radial stress p_r, radial strain u_r and tangential stress p_θ at the surface of the particle with three unknown scattering coefficients as schematically illustrated in Fig. 1(a). ρ, c, and k respectively denote the density, speed of sound, and wavenumber. Subscript 1, 2, L, and T respectively represent the surrounding liquid, particle, longitudinal mode and transverse mode. Note that although the shear wave contributions are considered in the theory, the visco-inertial interaction and thermal transport process are neglected, suggesting the applicable size would be limited to several microns in water. The validity of the Faran's theory

* Corresponding author.
E-mail address: nori@kit.jp (T. Norisuye).

http://dx.doi.org/10.1016/j.ultras.2015.05.016
0041-624X/

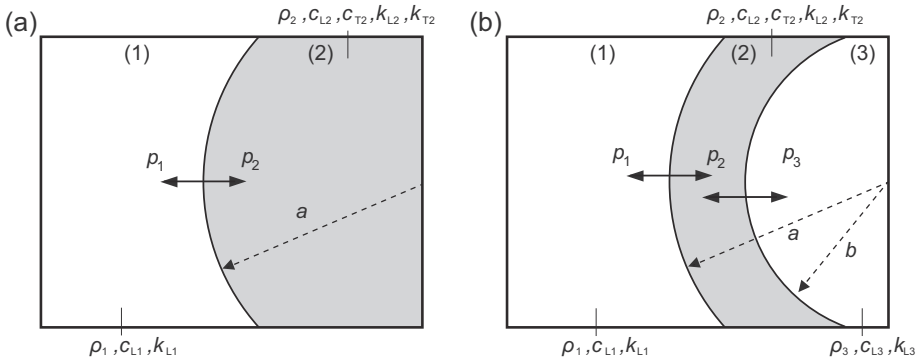

Fig. 1. Schematic representation of the scattering models for (a) hard sphere and (b) hollow particle.

was confirmed by Burke et al. [16] who observed the angular dependence of differential cross section of a single 0.635 mm steel sphere by 1–5 MHz transducers.

For a finite concentration of particles, multiple scattering [17–20] must be considered. The broadband frequency spectra of the attenuation coefficient and the sound velocity for suspensions of monodisperse polystyrene-rigid particles were studied by Mobley et al. [21,22]. The frequency dependences of the attenuation coefficient and the sound velocity for micro-particle suspensions were successfully reproduced by the scattering theory and the dispersion relation. As long as the scattering object is fluid, more simplified form proposed earlier by Anderson [23] could be used and the model seems to satisfactorily reproduce the experimental data for emulsions of fluorinated-oil droplets [24,25].

As the particle size becomes smaller, the thermal waves play an important role on the scattering behavior in addition to the longitudinal and shear waves. Epstein–Carhart [26] formulated a theory for liquid droplets dispersed in a viscous liquid, followed by generalization of the theory for solid particles dispersed in a viscous liquid by Allegra and Hawley [27]. Nowadays they are abbreviated as the ECAH theory by the combination of models. The extensive review can be found elsewhere [12,28]. While the ECAH theory does take into account the thermal wave contribution, the computation time takes longer because of the larger matrix with 3 more unknowns, and an idea to reduce the computation time is discussed in the literature [29]. On the other hand, the thermal wave contributions and the viscosity of liquid become negligible as the particle increases [30]. Therefore it is quite understandable that the attenuation data for micron-sized particles can be well reproduced by the Faran's scattering theory with the dispersion relation [22].

Acoustic scattering from hollow particles was considered by Junger [31] who derived the scattering function of air-filled elastic shell. Goodman and Stern [32,33] proposed an acoustic scattering theory of hollow particle immersed in an inviscid liquid for arbitrary shell thickness by solving the wave equations at the boundary conditions (Fig. 1(b)) similar to the method of rigid sphere. By solving the equations for the radial stress, radial strain and tangential stress at the inner and outer diameter, we obtain a 6 by 6 matrix about the scattering coefficient of the hollow particle. Since the theory assumed inner and outer fluids to be identical, a few modifications about the determinant of the matrix were attempted to generalize the model [34,35]. Suppose the shell thickness is sufficiently thin compared to the particle size and the shell part is soft enough to analyze the mechanical resonance, a model based on a gas bubble oscillation is also available [36,37]. The resonance frequency and the acoustic damping are studied for microbubbles encapsulated by a thin viscoelastic shell [38]. On the other hand, the validity of the scattering function approaches are not yet established, and at least the experimental evidence for the attenuation coefficient and the sound velocity of micro-particle in the micrometer range are obviously lacking. Therefore the objective of the study is to obtain the attenuation and the velocity spectra by ultrasound spectroscopy for versatile examples of particle suspension, and to demonstrate the validity of the scattering theory for the rigid and hollow particles in the micrometer range.

2. Experimental procedure

Standard polystyrene (PS) and polydivinylbenzene (PDVB) microspheres were respectively purchased from Moritex and Sekisui Chemical. Phenolic-resin hollow particles were purchased from Artisans Spirits. Hollow borosilicate particles (Fuji Balloon, S35) were supplied by courtesy of Fuji Silysia Chemical. The hollow particles were carefully fractionated by taking the upper fraction of the mixed solution after centrifugation while the broken fragments of particle collected at the bottom of the solution were eliminated prior to samples preparation. The particles were dispersed in an aqueous solution containing 0.2 wt.% sodium dodecyl sulfate (SDS) to obtain a suspension with desired concentrations in range $0.1 < C < 1\%$ in weight, followed by a brief immersion in a low power ultrasonic bath prior to ultrasound scattering experiments in order to avoid aggregation. Water was purified twice using 0.2 μm membrane filter after distillation. Disposal polystyrene rectangular vessels with the dimension $10 \times 10 \times 40\ mm^3$ and the wall thickness 1 mm were used as the sample cells.

An ultrasound pulse was generated using a broadband pulser/receiver (Olympus 5800PR) connected to a longitudinal plane wave transducer. Various water-immersion sensors having different nominal frequencies such as, iSL 0–3 composites (diameter 4 mm, 20 MHz) and KGK B30K1I (1 mm, 30 MHz) were employed to examine the frequency dependence of the sound velocity and attenuation coefficient of the materials. The transmitted pulse was received by another transducer, followed by amplification by the receiver. The sample cell and transducer was carefully aligned by a home-made stainless stage equipped with micro-step (x, y, z, α, β) stages. The signal was recorded by a 14 bit high-speed digitizer, GaGe CS-14200, with the sampling rate 200 Mega samples/s (for 20 MHz). A 12 bit digitizer, CS-12400 (400 Mega samples/s), was also employed to record the higher frequency data (30 MHz). The digital equipment was synchronized with a 10 MHz reference clock to avoid the phase jittering. The pulse repetition time was set at 0.5 ms and the pulse was averaged over 5000 times to achieve good statistics. The sample was set in a homemade thermostat bath regulated at 25 ± 0.01 °C.

SEM images (Hitachi S-3000N) were taken to verify the particle size and its distribution. Prior to observation, the samples were

Please cite this article in press as: K. Kubo et al., Sound velocity and attenuation coefficient of hard and hollow microparticle suspensions observed by ultrasound spectroscopy, Ultrasonics (2015), http://dx.doi.org/10.1016/j.ultras.2015.05.016