1P1-2

Studies on Viscoelasticity of Silicone-Elastomer Microparticles in Suspension Probed by Ultrasound Scattering Techniques

超音波散乱法によるシリコーンエラストマー微粒子の粘弾性に関する研究

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1. Introduction

Ultrasonic transmission Spectroscopy (US) is a nondestructive and non-contacting technique to evaluate the elasticity of particle dispersed in liquid. So far, a good agreement between the experiments and ultrasonic scattering theories was comfirmed for polystyrene particles and its derivatives[1]. However, beside the success in elastic particle suspensions as well as emulsions, the viscoelasticity of particle was not examied so far. In this study, crosslinked polydimethylsiloxane (PDMS) particles were prepared as a model system. Then, the viscoelasticity of the particles in suspension was determined by a novel viscoelastic ECAH analysis.

2. Experimental section

2.1 Samples

Crosslinked PDMS particles were prepared by condensation reaction of linear hydroxy terminated polydimethylsiloxane (HTPDMS) and tetraethyl orthosilicate (TEOS) in the presence of stannous octanoate (STO) as a catalyst. The TEOS concentrations were varied from 1 to 7wt% for HTPDMS (7 concentrations), while the STO concentration was fixed to be 3wt%. TEOS and STO were dissolved in HTPDMS. After complete dissolution, the solution was poured into 1.0wt% sodium dodecyl sulfate (SDS) aqueous solution. Then, the solution was stirred by a homogenizer for 10 minutes (3400 rpm), followed by further mixing for 48 hours by a magnetic stirrer (350 rpm).

After the crosslinking reaction, PDMS particles were fractionated by two types of filters (pore size : 10 and 20 μm). Finally, the PDMS particles were dispersed in the SDS aqueous solution. These particles were abbreviated as Cx1 - 7 representing the TEOS concentrations.

2.2 Ultrasonic transmission spectroscopy

A spike pulse emitted from a pulser was transferred to a longitudinal plane wave transducer immersed in a water bath to generate ultrasound pulses. The scattered signals were received by another transducer, followed by successive recording with a high-speed digitizer. The frequency dependences of the intensity attenuation coefficient α, and the phase velocity c, were acquired by US as illustrated in **Fig. 1**. They were analyzed using the relations,

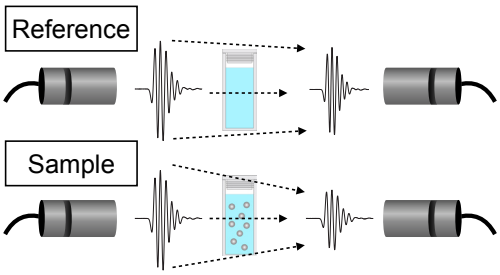

Fig. 1. Schematic representation of the experimental setup for ultrasonic transmission spectroscopy.

$$a_{\mathrm{sam}} = -\frac{2}{L}\left[\ln\left(\frac{|A^*_{\mathrm{sam}}|}{|A^*_{\mathrm{ref}}|}\right)\right] + a_{\mathrm{ref}} \qquad (1)$$

$$c_{\mathrm{sam}} = \frac{2\pi f L}{\theta_{\mathrm{sam}} - \theta_{\mathrm{ref}} + \frac{2\pi f L}{c_{\mathrm{ref}}}} \qquad (2)$$

where A is the amplitude, θ is the phase of the transmitted pulse and the subscript "sam" and "ref" respectively refer to the transmitted pulse for the sample and reference. L is the sample thickness.

Disposable polystyrene rectangular vessels with the dimension 10 × 10 × 40 mm^3 and the wall thickness 1 mm were used as the sample cells.

3. Results

The PDMS particles were imaged by using a phase-contrast optical microscope equipped with a CCD camera (**Fig. 2(a)**). The particle size distribution was obtained to evaluate the average particle size and the coefficient of variation CV as shown in **Fig. 2(b)**.

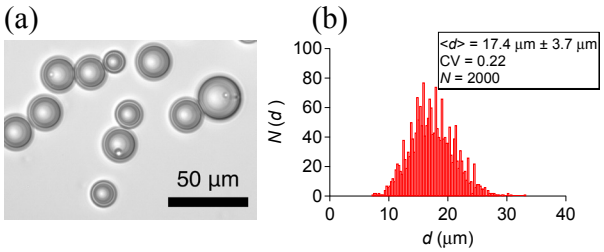

Fig. 2 (a) Optical micrograph of Cx1. (b) Particle size distribution obtained by a phase-contrast optical microscope.

Fig. 3 shows α and c of Cx1 - 7 suspensions as a function of frequency. Because the concentrations of all suspensions were fixed to be about 1.0wt%, changes in the α and c spectra were ascribed to the properties of the PDMS particle. **Fig. 4** shows the acoustic properties evaluated by the viscoelastic ECAH calculation for PDMS particles where c_L and c_S are the longitudinal and shear velocities respectively, and η is the shear viscosity. L' and G' are respectively the longitudinal and shear moduli with $L' = \rho c_L^2$, and $G' = \rho c_S^2$. G'' is the loss shear modulus where $G'' = \eta\omega$. In this study, the density, ρ and intrinsic absorption α/f^2 were determined by measurements of the sheet samples of each particle. **Table I** summarized the evaluated parameters.

Table I The density and intrinsic absorption of the PDMS sheets.

C_x (wt%)	ρ (g/cm^3)	$\alpha/f^2 \times 10^{-14}$ (s^2/cm)
1	0.973	1.23
2	0.974	1.40
3	0.974	1.45
4	0.976	1.60
5	0.981	1.58
6	0.986	1.73
7	0.990	1.84

Systematic changes in L' and G' as a function of C_x were clearly observed, while G'' was a weak function of C_x or rather invariant irrespective of C_x. It is known that the magnitude of G'' is larger than G' in the ultrasonic frequency range[2]. Evaluated G'' was on the same order of G' or larger than G' in accordance with the literature.

4. Conclusions

Ultrasonic transmission spectroscopy was employed to investigate the suspensions of PDMS particles. The crosslinker concentration dependence of the complex longitudinal and shear moduli were evaluated by the novel viscoelastic ECAH analysis. The relation of G' and G'' was consistent with the data obtained for the linear PDMS reported in the literature [2].

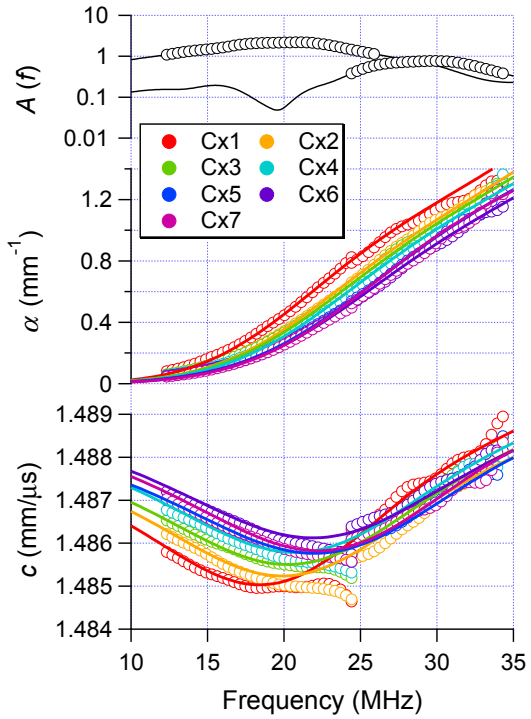

Fig. 3 Transmission amplitude of ultrasound pulse as a function of frequency using 20 and 30 MHz transducers, and frequency dependence of α and c of Cx1 - 7 suspensions.

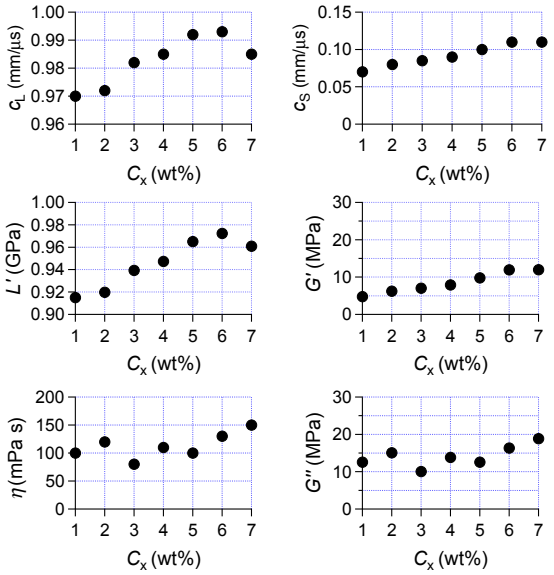

Fig. 4 The crosslinker concentration dependence of the mechanical properties.

References

[1] K. Kubo, et al., Ultrasonics **62** (2015) 186-194.
[2] Verdier. C et al., Rheol Acta **37** (1998) 234-244.