Fabrication of Polymer Particles via Emulsion Template and its Elasticity of Particle in Liquid Determined by Ultrasound Scattering Techniques

エマルションから析出させたポリマー微粒子の創製と溶液中の微粒子の力学特性解析

Kazuto Tsuji[1†] and Tomohisa Norisuye[1] ([1]Grad. School of Sci. & Tech., Kyoto Institute of Technology)

辻和人[1†]，則末智久[1] ([1]京工繊大院工)

1. Introduction

Ultrasonic transmission Spectroscopy (US) is a powerful tool to evaluate the mechanical properties and/or size distribution of particle dispersed in liquid. In the classical US analysis, the viscosity was considered for liquid droplets and the elasticity was considered for solid particles. On the contrary, both effects were taken into account in the previous study of the viscoelastic particle analysis[1]. In addition, the glass transition from liquid droplet to solid particle through evaporation of solvent was examined recently. For the chloroform droplet containing polystrerene (PS) and the toluene droplet containing PS, the glass transition concentrations were about 90vol% regardless of the type of solvent. This suggests that the critical volume fraction may be dependent on the polymer structure. Therefore, the behavior was examined using poly(2,6-dimethyl-1,4-phenylene oxide) (PDPO) whose glass transition temperarure is about 100°C higher than PS. Since PDPO is a rigid crystalline polymer, its structure could be drastically tuned by the heating temperature. In this study, the relationship between the heating temperature and elastic modulus of particles was investigated.

2. Experiments

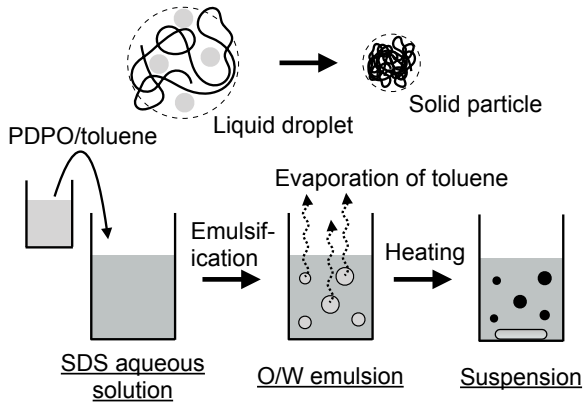

Fig. 1 Schematic illustration of the preparation method of the PDPO particles.

A PDPO powder was dissolved in toluene at 5wt% and aged for a few days to obtain the homogeneous solution. Then, the solution was emulsified in a 1.0wt% sodium dodecyl sulfate (SDS) aqueous solution. The oil-in-water (O/W) emulsion with the uniform size was prepared by using an internal pressure type micro-kit SPG emulsification system equipped with SPG membrane. The pore size of the SPG membrane was 15 μm. Then, the emulsion was stirred at 400 rpm for 24 hours under 25°C. The similar experiments were carried out at 58°C for 3 hours and 87 °C for 2 hours. The procedure is illustrated in **Fig. 1**. Since these particles contained a small amount of the aggregates with the size ranging from 50 μm to 1 mm, the particles were fractionated using a nylon mesh filter with the pore size 10 and 41 μm. Subsequently, the particles were purified with a large amount of water, followed by annealing at 110°C to obtain the dried powder.

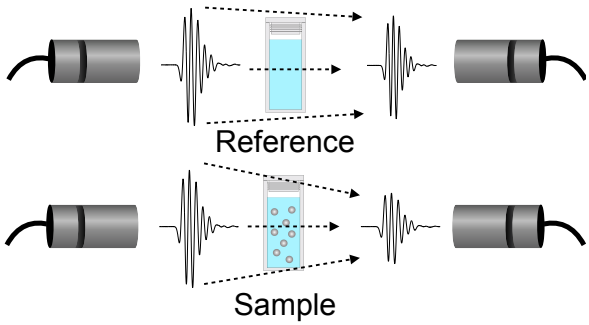

Fig. 2 Schematic representation of the experimental setup for ultrasonic transmission spectroscopy.

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. 2**. They were analyzed using the relations,

$$\alpha_{\mathrm{sam}}(f) = -\frac{2}{L}\left[\ln\frac{A_{\mathrm{sam}}(f)}{A_{\mathrm{ref}}(f)}\right] + \alpha_{\mathrm{ref}}(f) \qquad (1)$$

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

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

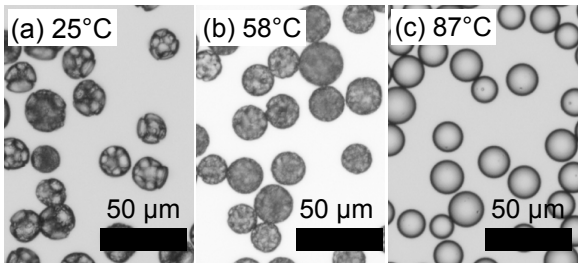

Fig. 3 The optical micrographs of the PDPO particles.

The PDPO particles were imaged using an optical microscope (Olympus, model CX43) equipped with a CCD camera (**Fig. 3**). These particles were respectively obtained by heating the emulsions at (a) 25°C, (b) 58°C, and (c) 87°C. The average particle diameters were about 20 μm irrespective of the evaporation temperature. As shown in the figure, porous structures were observed for (a) and (b). Thus, it is expected that the particle operated at 25°C has low elastic modulus due to the porous structure.

Fig. 4 shows the frequency spectra of attenuation coefficient α/f^2, and phase velocity c, obtained for the three kinds of the PDPO particles dispersed in water with a small amount of SDS. The concentrations of particle were (a) 0.28wt%, (b) 0.11wt%, and (c) 0.1wt%. The black circle represents SDS aq. without particle. The red circle, the green square, and the blue diamond represent the PDPO particle suspensions prepared at different temperatures. Quadrupole peaks of α/f^2 and c associated with the shear rigidity were respectively observed at 12, 28, and 32 MHz for the particle prepared at 25, 58, and 87°C. The solid, dotted, and broken lines indicate the theoretical curves

Table I The heating temperature, c_{L} and c_{S} of the PDPO particles.

Temperature (°C)	c_{L} (m/s)	c_{S} (m/s)
25	2,000	400
58	2,100	930
87	2,200	1,020

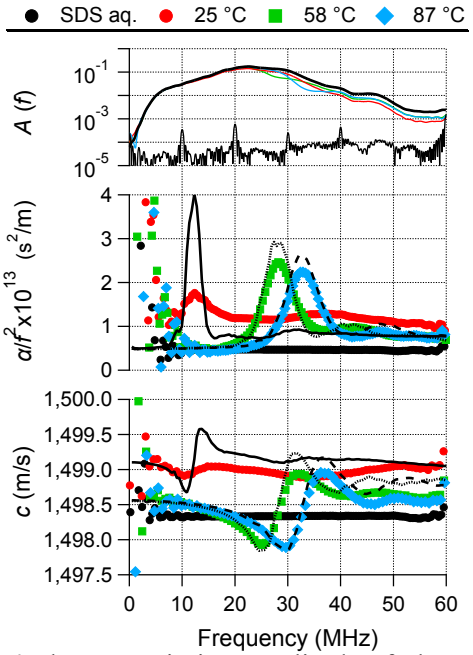

Fig. 4 The transmission amplitude of ultrasound pulse as a function of frequency $A(f)$ and the frequency dependences of α/f^2 and c of the PDPO particle suspensions. The experimental data (markers) and the theoretical calculations (lines).

calculated by the ECAH theory[2], [3] with the dispersion relation of Lloyd-Berry[4]. Although none of the parameters could give exact matching of the theory with the experimental data, the shear velocity was determined by adjusting the location of peak. The acoustic parameters used in the ECAH calculation of the PDPO particles, such as longitudinal velocity c_{L} and shear velocity c_{S} were summarized in **Table I**. The particle evaporated at 25°C exhibited the lowest shear modulus (shear velocity), which is in agreement with the finding given in Fig. 3.

4. Conclusions

The PDPO particles having various structures were fabricated by evaporating toluene from the PDPO/toluene droplets in SDS aqueous solution. It was found that the elastic modulus of the particle prepared at the different temperatures were correlated with the structures observed by optical micrograph.

References

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