Resonance Scattering Analysis of Viscoelastic Particles in suspension using Ultrasonic Spectroscopy Method

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1. Introduction

When an ultrasound pulse is impinged to a suspension of liquid droplets or solid particles dispersed in water, ultrasonic scattering from the particles occurs. The frequency dependence of the ultrasonic attenuation coefficient and phase sound velocity of the microparticle suspensions can be obtained by measuring the amplitude and phase of these pulses. By analyzing these frequency spectra using a scattering theory, the particle size distribution and the mechanical properties can be calculated. The ECAH theory, developed by Epstein, Carhart, Allegra and Hawley, describes the scattering behavior of microparticles dispersed in liquid with viscous and thermal dissipation[1, 2]. By predicting attenuation coefficient and phase sound velocities based on the scattering coefficients predicted from the theory and comparing the frequency spectra with experimental values, the elastic moduli of particles can be evaluated for a variety of particles ranging from nanoparticles to micron-sized particles[3]. Note that, to reduce ambiguity of the analysis, either the particle size distribution or the elastic modulus should be known. In the ECAH analysis, the shear viscosity was considered to liquid droplets and the shear elasticity was considered to solid particles. However, no quantitative analysis of viscoelastic microparticles considering both elasticity and viscous loss simultaneously has ever been performed.

Recently, we have performed viscoelastic analysis of the elastic modulus and viscous loss of individual microparticles dispersed in water and proposed a new viscoelastic ECAH analysis method for materials showing significant viscous loss, such as elastomer particles of cross-linked polydimethylsiloxane and high-impact polycarbonate particles, and have shown its validity [4]. However, the examples are limited to the aforementioned samples, and there is a lack of knowledge on the mechanism of the appearance of viscous loss. Therefore, the purpose of this study is to investigate the acoustical properties of microparticles with different glass transition temperatures (T_g), and to verify the validity by comparing the thermal and mechanical properties.

2. Experimental section

2.1 Sample

To prepare particles with different T_g, poly(2-ethylhexyl acrylate) (PEHA), poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(n-butyl methacrylate) (PBMA), polystyrene (PS) and poly(methyl methacrylate) (PMMA) were dissolved in toluene. Then, aqueous emulsions with these polymer solutions (oil phase) were prepared by using Shirasu Porous Glass (SPG) emulsification system equipped with a SPG membrane. The pore size of the membrane was 15 μm. The diameter of the particles immediately after emulsification was 50 μm, but as the toluene in the droplet evaporated, the particle size decreased, eventually reaching 20 μm.

2.2 Ultrasonic Spectroscopy Method

Two broadband longitudinal ultrasonic transducers manufactured by KGK with a nominal center frequency of 20 MHz were placed in water controlled at 25.000 ± 0.005°C. An ultrasonic pulse transmitted through a sample cell was received by another transducer. The cells were disposable PS cells with a cell window thickness of about 1 mm and a path length of about 10 mm were employed. The distance between transducers was set at an optimal distance to minimize the effect of edge waves. For a 20 MHz transducer with a 2 mm element diameter, the distance between transducers is about 10 cm.

For excitation, a DPR500 manufactured by JSR and a remote pulser RP-H4 were used to apply spike waves to the transducer. The typical excitation voltage was –330 V, the applied energy was about 2 μJ, and the damping was 50 Ω. Ultrasound pulses transmitted through the cell were received by another transducer and recorded on a high-speed digitizer board (CS12400) with a bit depth of 12 bit and temporal resolution of 400 megasamples per second. The transmitted waves of the sample and the reference (pure water) were Fourier transformed, and the frequency dependence of the ultrasonic attenuation coefficient and phase sound velocity were obtained from the amplitude ratio and phase difference of the transmitted waves, respectively. The particle size distribution was

obtained by analyzing images taken in bright field with an Olympus CX-43 optical microscope equipped with a 10x objective lens.

3. Results

Fig. 1 shows the frequency, f dependence of ultrasonic attenuation coeffisient, α obtained for PEHA, PEA, PMA, PBMA, PS, and PMMA. The solid lines are calculated values obtained by the ultrasonic scattering analysis combined with the ECAH theory, based on the given physical properties for the dispersed and continuous phase. Viscous loss and shear velocity of the particle were examined for values that best match the experimental data. The resonant scattering peaks, characteristic of solid particles, are seen at 23, 36, 29, 34 and 42 MHz, respectively, for PEA, PMA, PBMA, PS, PMMA. PEHA will be mentioned later. The peak frequency appears at a lower frequency for larger particles, and in this experiment, the particle diameter was kept constant at 20 μm for all the samples. Therefore, the difference in the peak position is thought to be due to the difference in the elastic modulus of the particles. The peak of PEA (T_g=–16°C, measured by differential scanning calorimetry (DSC)), has a broad spectrum compared to other types of particles, which is quite different from the dotted line without considering viscoelastic effects. η_2=1,200 mPa·s was obtained as the viscosity parameter that satisfies the frequency spectrum of the attenuation coefficient and phase sound velocity of PEA. In addition, PEHA has a lower T_g than PEA, which is estimated to contribute more to its viscosity, η_2=2,000 mPa·s, making its spectrum broader than that of PEA.

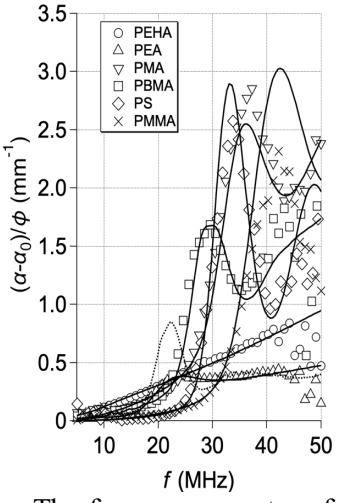

Fig. 1 The frequency spectra of α obtained for the polymer particle suspensions.

Fig. 2 shows the T_g dependence of the longitudinal sound velocity c_{L2}, shear velocity c_{S2}, viscosity coefficient η_2, longitudinal wave attenuation coefficient α_2/f^2, and density ρ_2 for polymer particles obtained by the ECAH analysis. For example, for PS particles, c_{L2}=2,328 m/s、c_{S2}=1,164 m/s、α_2/f^2=2×10^{-13} Np·s^2/m、η_2=0 mPa·s、ρ_2=1,045 kg/m^3. The value of shear velocity, which is directly related to the shear modulus of the polymer particles, increases with increasing T_g, allowing us to evaluate the stiffness and softness of the polymer particles in the ultrasonic frequency band. Furthermore, the viscoelasticity of the polymer particles also tends to be well captured with T_g, as the viscous part appears as a parameter from T_g considerably lower than room temperature (25°C) to near room temperature.

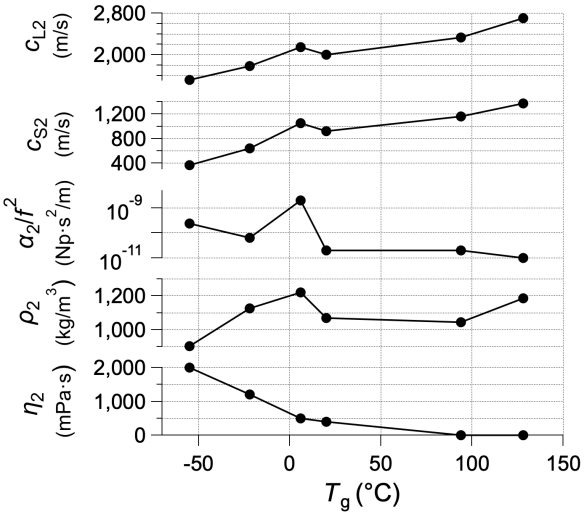

Fig. 2 T_g dependence of c_{L2}, c_{S2}, α_2/f^2, η_2, ρ_2.

4. Conclusions

For viscoelastic particles in suspensions measured by ultrasonic spectroscopy, quantitative scattering spectral analysis of the particles, which simultaneously considers both shear viscosity and shear elasticity, was enabled to evaluate the physical properties of polymer particles with different glass transition temperature.

References

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