

Emergence of Shear Wave Viscoelasticity with Drying of Droplet Observed by Longitudinal Ultrasonic Scattering Method

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1. Introduction

Ultrasonic spectroscopy (US) method combining the particle scattering theories is a nondestructive and non-contacting method for measuring the size and elastic properties of nano- to micro-sized particles. The technique was further developed to allow in-situ analysis during the particle synthesis and/or liquid drying process of emulsion where the liquid droplet transformed into glassy particle through the intermediate viscoelastic regime^{1,2)}.

One of the most important properties of polymers is viscoelasticity. Polymers behave as rigid glass at low temperatures and soft rubber at high temperatures, and significantly change mechanical and dynamic properties. The ECAH theory, which is one of the ultrasonic scattering theories enables us to evaluate the physical properties of particles in suspension^{3,4)}. While the viscosity and the elasticity of particles has been considered independently for liquid and solid in the standard conventional ECAH theory, the viscoelastic ECAH analysis, which incorporates both viscosity and elasticity was developed in our laboratory²⁾. This allows us to evaluate the elastic modulus of a single particle in a suspension. In fact, the experimental data obtained for polycarbonate (PC) and polydimethylsiloxane (PDMS) particle, both well-known impact-resistant materials, have indicated that viscous effects were crucial in addition to the elastic contribution.

Besides above examples, polymers with various glass transition temperatures (T_g) were not sufficiently tested. Therefore, the purpose of this study is to clarify the glass transition behavior by probing the change in the shear velocity and loss-modulus during the drying process of liquid droplet in water with different T_g s by using the US method.

2. Experimental section

2.1 Sample

Poly(2-ethylhexyl acrylate) (PEHA, $T_g = -71^\circ\text{C}$), poly(ethyl acrylate) (PEA, $T_g = -16^\circ\text{C}$), poly(*n*-butyl methacrylate) (PBMA, $T_g = 24^\circ\text{C}$) and polystyrene (PS, $T_g = 94^\circ\text{C}$) were used. These polymers were dissolved in toluene to prepare 12wt% toluene solutions as the oil phase, and

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 droplets immediately after emulsification was 50 μm , but as the toluene in the droplet evaporated, the particle size decreased and eventually reached 25 μm . Also, the T_g of each polymer was measured by differential scanning calorimetry (DSC).

2.2 Ultrasonic Spectroscopy Method

Two broadband longitudinal ultrasonic transducers manufactured by KGK were placed facing together in water tank. In this study, two couples of transducers with different central frequencies, 5 MHz and 20 MHz are employed to simultaneously capture the drying process of liquid droplets over a wide range of frequency. These four transducers were carefully aligned using a custom-made dual-stage, which allows us to capture the glass-transition behavior in a single droplet over the wide range of frequency. The thermostatic water bath was controlled at $25 \pm 0.005^\circ\text{C}$. A poly(phenylene sulfide) cell was placed in the middle of the transducers and the transmitted waves of the ultrasonic pulses were analyzed.

For excitation, a DPR500 manufactured by JSR and remote pulsers RP-L2 (5 MHz) and RP-H4 (20 MHz) were used. Ultrasonic pulses transmitted through the cell were received by another transducer and recorded on a high-speed digitizer board (CSE1622) with a bit depth of 16 bits and temporal resolution of 200 megasamples per second. The particle size distributions were obtained by analyzing images taken in bright field using a Nikon OPTIPHOT-2 optical microscope equipped with a 10x objective lens.

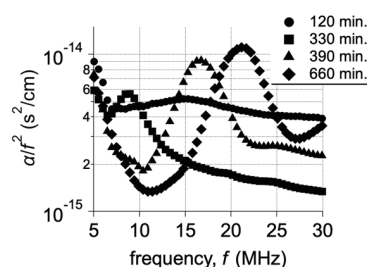


Fig. 1 Frequency dependence of the attenuation coefficient of the PBMA/toluene emulsion during the drying process.

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3. Results

Fig. 1 shows the frequency dependences of the attenuation coefficient of the PBMA/toluene emulsions obtained by the US method during the drying process. In the initial stage of drying at 120 min. after emulsification, the PBMA concentration in the PBMA/toluene droplets was low. Thus, a broad peak (monopole peak) is observed indicating that the droplet is liquid. As the toluene evaporates after 330 min., a noticeable quadrupole peak, which is a representative of solid resonance was observed at 8 MHz. At this point, the particles are probably in intermediate regime of viscoelasticity, thereby the peak is fairly broadened. However, as the toluene evaporates, the peak shifts to higher frequencies (390 min.), and eventually appears at 21 MHz (660 min.).

Next, all the spectra obtained from the drying process of the PBMA/toluene emulsion were analyzed using the viscoelastic ECAH theory, and the results are shown in **Fig. 2**. The vertical axes are, from top to bottom, the parameters of longitudinal sound velocity c_{L2} , shear sound velocity c_{S2} , longitudinal attenuation coefficient $a_2 f^2$, shear viscosity coefficient η_2 , and density ρ_2 . The c_{L2} was initially close to the velocity of toluene, but gradually solidifies and finally shows the same velocity with the bulk. Although the c_{S2} was 0 for liquid, as the toluene evaporates, it increased with drying time, representing the solid nature of particle where the onset of elasticity was observed at $T = 300$ min. Correspondingly, shear viscosity η_2 also showed a maximum at $T = 300$ min.

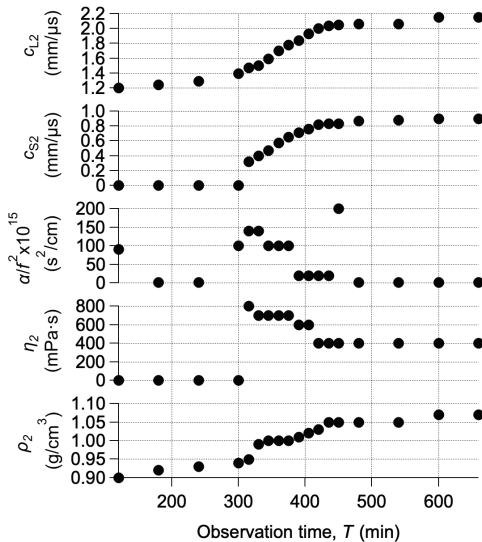


Fig. 2 Results of viscoelastic ECAH theory analysis of the PBMA/toluene emulsion during drying process.

Similar experiments were performed for the PS, PEHA and PEA droplets. The results are shown in **Fig. 3 and 4**. Note that volume fraction ϕ was calculated from the change in particle size over

drying time.

Fig. 3 shows ϕ dependence of c_{S2} normalized by that of bulk polymer. The glass transition concentration C_g is defined as the point where c_{S2} rises rapidly. The location of C_g was confirmed to be in the order of T_g of polymer, i.e., PS, PBMA, and PEA. Although PEHA has a lower T_g than PEA, c_{S2} of PEHA rises faster than PEA, thus exhibited a lower C_g . In addition, **Fig. 4** shows that η_2 increases around C_g for all the polymers, but the peak of viscosity appears at a higher ϕ for PEHA than for PEA. These phenomena might be attributed to the difference in molecular structure (molecular chain mobility) between PEA and PEHA.

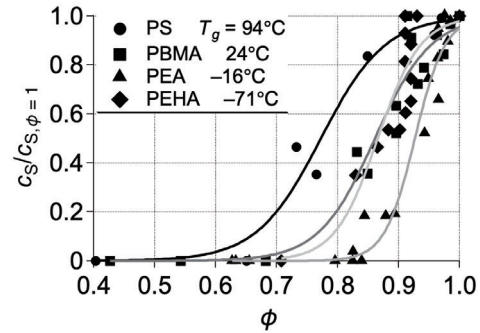


Fig. 3 ϕ -dependence of c_{S2} in each polymer.

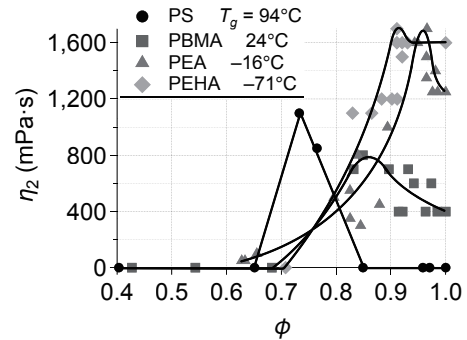


Fig. 4 ϕ -dependence of η_2 in each polymer.

4. Conclusions

US method combining the viscoelastic ECAH analysis revealed the formation of glassy particle through the solvent evaporation process. In this study, various types of polymers having different T_g were tested. The analysis successfully extracted the viscoelastic nature of particle dispersed in liquid where they exhibited intermediate properties between liquid viscosity and solid elasticity.

References

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