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Analysis of Size and Viscoelasticity of Waterborne-Polyurethane Nanoparticles by Ultrasonic Scattering Method

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1. Introduction

Polyurethane (PU) is widely used in building, furniture, packaging, and automotive products, including coating, adhesive and binder materials. In recent years, increasing environmental awareness has led to the active development of waterborne polyurethane (WBPU) materials that do not emit organic solvents into the atmosphere[1)]. In particular, film-forming ability of WBPU nanoparticle and excellent adhesion to different kinds of materials have accelerated the development of WBPU nanoparticle dispersion for versatile industrial applications. In general, however, they are almost never used under dilute concentration conditions, as in basic research, but are often used at very high concentrations.

Ultrasonic scattering is a useful method to investigate the dispersion state and physical properties of particle suspensions. As the size and/or concentration of the particles becomes larger, transmission of visible light may not be allowed. In such cases, ultrasonic scattering method can be a good candidate as an alternative technique to the optical method.

In general, an ultrasonic single-scattering model is extended and combined with a dispersion relation that accounts for multiple scattering to achieve very high concentrations. However, most models assume droplets dispersed in a liquid, i.e., an emulsion. Even in these cases, the concentration is limited to about 30 vol% at most. In particular, concentrated systems of solid particles are even more difficult to analyze because of the mode conversion from longitudinal to shear waves which are inherent in solids. For example, the ECAH theory[2, 3)] developed by Epstein, Carhart, Allegra and Hawley describe the single scattering behavior of microparticles dispersed in a liquid, and considers the so-called mode conversion, in which part of the incident longitudinal wave is dissipated as viscosity or heat.

Recent theories have also proposed models that consider multiple scattering of shear waves, in which an incident longitudinal wave is converted to a shear wave mode and then further converted again from a shear wave to a longitudinal wave mode. In this study, as described above, ultrasonic analysis considering multimode multiple scattering was performed for WBPU microparticle dispersions, and furthermore, the physical properties of the WBPU particulates in water affected by the water content and swelling of the WBPU particulates in water were discussed.

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2. Experiment

2.1 Synthesis of WBPU particles

A linear polyurethane, waterborne polyurethane (WBPU), was synthesized by reacting isophorone diisocyanate (IPDI), polypropylene glycol (PPG), 2,2-bis(hydroxymethyl)propionic acid (DMPA), triethylamine (TEA), and 1,4 butanediol (BD) in acetone solvent. To examine the physical properties of WBPU, the bulk sheets were prepared by casting in petri dishes. Linear WBPU particles were prepared by adding pure water to a 75wt% WBPU acetone solution of the bulk (phase inversion method).

Cross-linked WBPU particles were similarly obtained by preparing a bulk WBPU acetone solution, then adding pure water with 3-aminopropyltriethoxysilane (APTES)[4)]. Cross-linked WBPU sheets were prepared by drying the solvent from the cross-linked WBPU particles.

Particle size was controlled by varying the amount of DMPA, TEA, and BD added during polymerization. Particle diameters were determined using an ELSZ-1000, Otsuka Electronics, Japan. The particles were dialyzed for up to 60 hours to purify the particles and were used as the measurement sample.

2.2 Ultrasonic Spectroscopy

As shown in **Fig. 1**, broadband longitudinal ultrasonic transducers manufactured by KGK were placed facing each other in water with low ultrasonic attenuation and a sample cell was placed in the

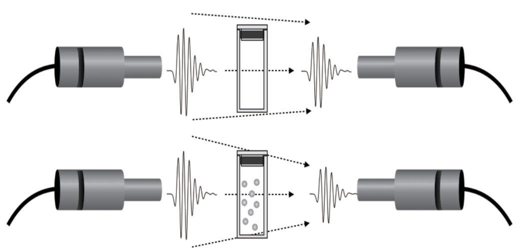

Fig. 1 Schematic representation of the experimental setup for ultrasonic transmission spectroscopy.

middle to analyze the transmitted waves of ultrasonic pulses. A disposable polystyrene cell was used as the cell. The thickness of the cell window is about 1 mm and the path length is about 10 mm.

3. Result

Fig. 2 shows the frequency f dependence of the ultrasonic attenuation coefficient α/f^2 and phase velocity c for the linear and cross-linked WBPU sheets obtained by ultrasonic spectroscopy. Both α/f^2 and c were slightly larger for the linear WBPU sheet than the cross-linked WBPU sheet. The meaning of the solid markers will be explained later.

Ultrasonic scattering analysis of WBPU particles dispersed in liquid was then performed. **Fig. 3** shows the results of the concentration dependence of α and c for WBPU particles at 10 MHz. The solid gray line is the calculated line based on the ECAH theory without considering heat dissipation, and the solid black line is the theoretical calculation based on the ECAH theory considering thermal wave.

Without considering mode conversion to thermal waves, the calculated results were close to the experimental results for the linear WBPU particles with a diameter of 240 nm, but the theoretical values were comparable regardless of particle diameter. The mode conversion to thermal waves was considered to be more important for smaller particle diameters, resulting in larger attenuation coefficient and smaller phase velocity. The effect of the theoretical particle diameter became more pronounced, but rather far from the experimental values. Therefore, leaving the phase velocity and attenuation coefficient of the continuous phase (pure water) unchanged, we determined α/f^2 and c for the particle component that satisfied the experimental values of suspension. The results are plotted in Fig. 2 by solid markers.

The α/f^2 of the particles was slightly smaller than the sheet value. This may be due to the affinity of WBPU for water, which may cause the particles to swell in water. On the other hand, the phase velocity was significantly different from the sheet value, being close for submicron particles of 240 nm, but becoming larger as the particle size decreased to 140 nm and 45 nm. This may be because the smaller nanoparticles are more easily penetrated by water to the center, and the dissociation of charge of DMPA introduced during the synthesis process, increasing the bulk elastic modulus.

4. Conclusions

Ultrasonic properties of waterborne polyurethane particles were analyzed by ultrasonic spectroscopy. It was found that the submicron particles showed values close to the bulk properties, while the nanoparticles exhibited a high longitudinal modulus and a small attenuation coefficient.

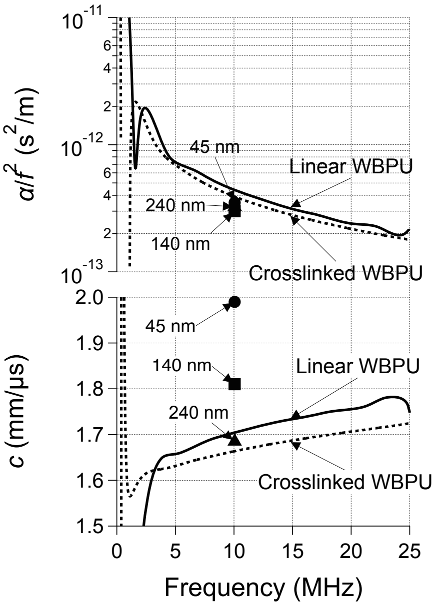

Fig. 2 The frequency dependences of α/f^2 and c of the WBPU bulk sheets.

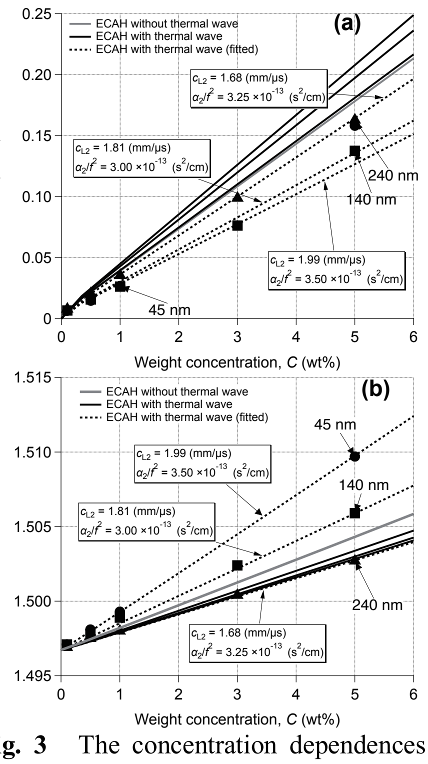

Fig. 3 The concentration dependences of α and c of the WBPU dispersions.

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