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Effect of concentration condition in microencapsulation and gelation of sodium alginate on viscosity behavior of gel-like particle dispersion

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1. Introduction

The viscosity and/or viscoelasticity are the fundamental mechanical properties determining the hydrodynamic response. For example, they are needed to calculate the stress applied to a pipe wall and the pressure loss due to flow. Even for a complex situation for which the Navier-Stokes equation cannot be solved, it is possible to predict the time evolution of fluid motion with using them as a main parameter for numerical simulation. Therefore, the viscous and/or viscoelastic properties are in high demand for all industrial fields that handle fluids.

On the other hand, their properties are also the physical quantities reflecting the dissipation and propagation of energy. Namely, they have the possibility of changing according to the number of degrees of freedom of microscopic molecular motion as well as the magnitude of interactions between degrees of freedom. To have such characteristics, in most cases, they show relaxation or resonance phenomena with respect to frequency. Thus, spectroscopic study is a useful tool to reveal hydrodynamic behavior from the view point of an academic interest.

Blood is a typical dense system, where red blood cells (RBCs) are dispersed in aqueous solution including some ions and proteins. Since the RBCs have some soft and flexible characters, the viscosity of blood shows an interesting non-Newtonian behavior such as shear thinning [1,2)]. We note that the mechanical properties of RBCs can be obtained by analyzing the degrees of shear thinning behavior. Here, the shear thinning means that the viscosity decreases with increasing the shear rate, which is the same as the velocity gradient. As the shear rate has the unit of inverse of seconds, the shear thinning is similar to a relaxation behavior of viscosity depending on the ultrasonic frequency.

The typical value of viscosity for human bloods becomes only several to 10 times higher than that of water. It is extraordinary that a lowly viscous fluid has a clear tendency of shear thinning during the range of shear rate of 20 to 600 s^{-1}, which corresponds to the actual blood flow through the thickest to thinnest vessels in human body. In order to investigate viscosity curve in detail, a rotational-type rheometer must be the first candidate. However, most commercially available rheometers have insufficient accuracy in measuring low viscosity less than 10 mPa·s.

Recently, the authors have developed a rheometry system equipped with the Electro-Magnetically Spinning (EMS) method[3,4)]. This EMS rheometer is a torque-controlled rotational-type device in noncontact manner, and then achieves the more accurate measurement rather than conventional high-end rheometers. In addition, a sealed condition, easy temperature control, and disposable usage are feasible owing to the noncontact technique, and also a contamination-free operation for preparing and removing samples is available. These features might be a powerful tool for examining large number of blood samples without spending time and cost.

The final goal of this study is to obtain the quantitative data about the mechanical properties of RBCs. It is preferred in the initial step towards achieving this goal to use an aqueous dispersion of microparticles covered with soft membrane as the model sample. There are, however, no commercial products satisfying such a request, and then, the authors tried to airborne fabricate a salmon roe-like structure with the 10 micron-order diameters by using originally developed inkjet technique[4,5)].

In this presentation, our microencapsulation technique is introduced, and difference in viscosity curves depending on each concentration conditions of main and curing agents for gelation is investigated. In addition, a clear change of shear thinning behavior due to application of ultrasonic wave to the sample solution is discussed.

2. Sample preparation

A schematic form of RBCs can be regarded as a capsular structure containing an inner aqueous solution and an outer gel-like membrane. Then, a microparticle of artificial roe will be useful as a substitute for RBCs. The raw materials are two aqueous solutions of sodium alginates and calcium chlorides. The former is the main material forming gel networks, and the latter is the curing agent for cross-linking reaction.

Both solutions are ejected into the air as microdroplets with the synchronized frequency so that each droplet of different solutions collides one by one, which are shown as Fig.1. To spontaneously generate capsular structures due to the Marangoni

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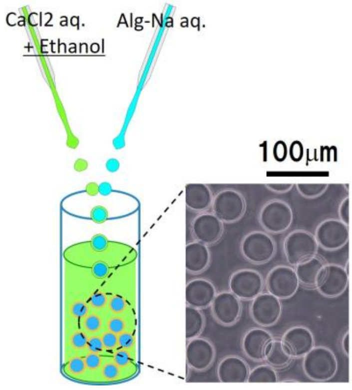

Fig. 1 Schematic image of microencapsulation by using an inkjet technique and microscope image of the fabricated particles.

effect resulting from the balance of surface and interfacial tensions, ethanol is added only in the solution of calcium chlorides. In fact, a distorted and unfinished structure was obtained when using the solution that does not contain ethanol.

Gelation reaction progresses at the contacting area towards the inside during airborne flying. The flying particles are finally caught by sufficiently large amount of distilled water in a test tube. Figure1 also shows a photo image of generated particles. It can be confirmed that microparticles with almost uniform diameters are dispersed individually.

The key feature of this self-made aqueous dispersion is to show sedimentation and redispersion properties similar to those of blood. The dispersion sample is separated into two parts; condensation layer of particles and supernatant liquid, after still-standing for several minutes. Then, the separated sample can be reverted to the homogenous state just by stirring. Therefore, the volume occupation ratio of the sample is readily adjusted by increasing or decreasing the volume of the supernatant liquid.

3. Viscosity curve measurements

The viscosity curves were measured with the EMS rheometry device using an auto-balancing rotor (ABR20003-ALE, TRIPLE EYE). In this type of setups, the sample volume should not be too much or little. The appropriate volume is about 0.5 ml, which is acceptable to future practical usage for medical test of blood. All the measurements were conducted with sweeping shear rate from high to low after the pre-shear process, in which a few minutes of high shear flow was applied to the set sample.

Figure 2 shows the series of measurement data for some concentration solution of calcium chloride, which works as curing agent for gelation. There is significant difference in the degrees of viscosity modulation, and then, larger change was verified for higher concentration up to 9 %. However, the 12% solution has lower viscosity than the 9% solution. It

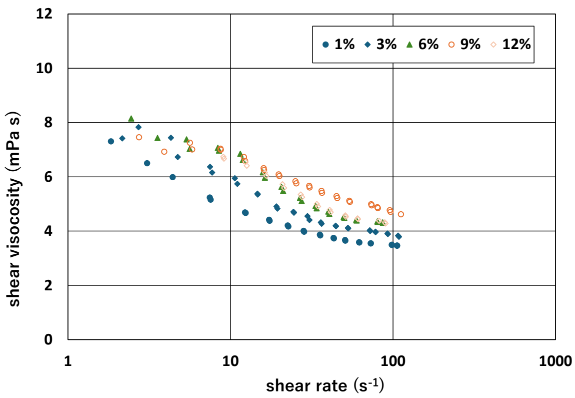

Fig. 2 Change of the obtained viscosity curves for the originally made gel-like particle dispersion depending on the concentration of curing agents.

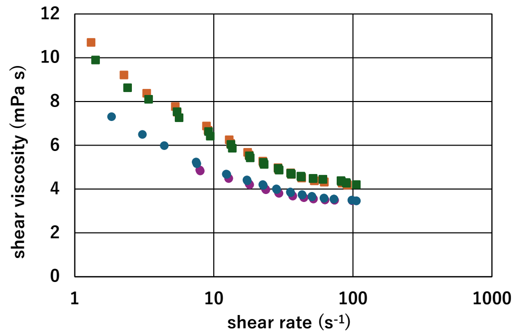

Fig.3 Compared results of the viscosity curves for different sample with or without ultrasound application to the main agent solution before gelation.

indicates that the excess of curing agent affects the hardness of gel-like structure. Recently, the material properties of alginate gel can be changed by applying ultrasound to the alginate solution before gelation reaction. The difference in curve shape of shear thinning, as shown in Fig. 3, will be discussed in detail at the symposium.

References

1) K. Furukawa, T. Abumiya, K. Sakai, M. Hirano, T. Osanai, H. Shichinohe, N. Nakayama, K. Kazumata, K. Hida, and K. Houkin, J. Stroke Cerebrovasc. Dis. **25,** 2762 (2016).
2) T. Hirano, S. Mitani, and K. Sakai, Jpn. J. Appl. Phys. **58**, SGGA03 (2019).
3) S. Mitani, M. Hirano, T. Hirano, and K. Sakai, Annu. Trans. Nord. Rheol. Soc. **25**, 329 (2017).
4) T.Hirano, S.Mitani, and K.Sakai, Jpn. J. Appl. Phys., 59, SKKA01 (2020).
5) D. Hayakawa, T. Hirano. S.MIitani, and K. Sakai, Jpn. J. Appl. Phys. **56**, 07JB02 (2017).