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ORIGINAL CONTRIBUTION

Preparation of spheroidal and ellipsoidal particles from spherical polymer particles by extension of polymer film

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Abstract Generation of particles of various sizes and shapes can be of great interest to scientists and engineers. We have developed a new and robust apparatus which can generate oblate spheroids from spherical polymer particles. A sheet of film dispersed with spherical particles was held by an eight-jaw extensional apparatus. The jaws were positioned in the edges of a regular octagon and moved radially to induce biaxial extension in an oil bath above the glass transition temperatures of the film and particles. We have demonstrated that polystyrene particles dispersed in a polyvinyl alcohol film can be stretched to generate various shapes by this method. The microscopic studies show that the oblate spheroids obtained by this method are virtually exact spheroids without showing knife edges. Also depending on positions with regard to holders, ellipsoids and even prolate spheroids can be obtained. The method has been found to be robust in that the deformation is always reproducible regardless of film thickness and very small deformation can be applied for nearly spherical particles. We have confirmed that this method can be applied for particles of submicrons to 10 μm in diameter or even larger ones. It is expected that the spheroids and ellipsoids obtained by this method can be of help in many studies including colloids, suspension rheology, electrophoresis, printed electronics, and pharmaceutical science.

Keywords Eight jaws · Biaxial extension · Spheroid · Ellipsoid

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Introduction

The spheroid particles can be of great interest to scientists and engineers for fundamental studies and applications. For example, suspensions made of spheroids should have vastly different rheological properties than those of spherical particles [1, 2]. In composite materials the microstructure is a strong function of particle shape [3, 4]. In pharmaceutical science, it has been reported that the most basic function of particles, degradation to release therapeutic drug, depends on particle shape [5, 6]. In electrophoresis of a particle, particle shape is one of the most important factors that determine the velocity of the particle [7–10]. In drying of an inkjet droplet with suspended particles on a solid surface, depending on particle shape, the drying pattern can be different [11] and the different drying pattern can result in the change in sharpness [12] of the image or different electrical properties in printed electronics [13–15].

The method of generating prolate spheroids was reported first almost two decades ago [16]. This method is based on the uniaxial extension of a polymer film which contains spherical polymer particles: The polymer film is elongated in one direction at above the glass transition temperatures of the film and the polymer particle. Champion et al. [5, 6] reported the extension of film in two orthogonal directions to generate oblate spheroids. However they reported only the basic concepts and the detailed information such as the exact shape or the yield of the process is not known. To utilize the particles practically not only the shape of the particles but also the easiness and productivity of the process is very important when a large amount of deformed particles is required. Therefore a more detailed study seems to be required to analyze the method for practical purposes. Recently Hu et al. [17] devised a blown film process to generate polymer spheroids. They mounted the polymer film with spherical particles onto a

funnel by bending the film at the edge of the funnel and blow a proper amount of gas to extend the film biaxially. Even though this method seems very useful in the production of oblate spheroids because the biaxial deformation is expected to be more homogeneous than the method used by Champion et al., it has some difficulties. Especially we have found that it was difficult to mount a thick film onto the funnel by bending at the right angle, which could cause air leak and nonuniform deformation. Also since the amount of extension has to be determined by the air pressure, the proper value of which has to be dependent on film thickness, it was not easy to determine the proper level of air pressure a priori and the air pressure has to be determined by a trial-and-error method to obtain the desired aspect ratio. Another problem of the blown film method was that it was very difficult to apply a small pressure difference with precision control at the high temperature to obtain oblate spheroids with an aspect ratio near one. The latter two problems can be overcome by applying a predetermined magnitude of biaxial extension to the film. Considering these points, we have developed a robust method to extend a polymer film in eight directions to generate biaxial deformation of the film and hence the production of oblate spheroids. In addition to the robustness of the method there was serendipity in that we have been able to obtain ellipsoids and even prolate spheroids.

Experiments

Particle synthesis

Polystyrene (PS) spheres of 2 μm in diameter were synthesized by the dispersion polymerization. PS spheres of 520 nm were synthesized by the surfactant-free emulsion polymerization. In two cases we have followed the procedures in the literatures strictly [18, 19]. Since the purpose of the present research is the shaping of particles, the detailed procedure on particle synthesis is omitted here. The weight molecular weights of PS of 2 μm and 520 nm were found to be 64,000 and 160,000 Da, respectively. The glass transition temperatures of PS of 64,000 and 160,000 are estimated to be 97 and 99 °C, respectively [20]. In Fig. 1, scanning electron microscopic images of the particles before deformation are shown. Particle sizes are virtually monodisperse even though the particle size varied slightly depending on batches. Since the extension method did not have any relation with the particle size distribution, no further investigation was performed on the quantitative distribution of particle size.

Film formation and extension

PS suspensions were prepared by dispersing PS particles in the aqueous solution of polyvinyl alcohol (PVA). PVA was purchased from Daejung Chem. Co. and had a degree of polymerization of 1,500. To prepare a sheet of 3 g of PVA was added to 40 ml of distilled water and the mixture was stirred for 24 h in a magnetic stirrer. To make the film softer after drying, 3 ml of 2 % glycerin solution in water was also added to the PVA solution as a plasticizer. The particle loading was 0.47 %. To have more particles per batch, the particle concentration could be larger. But if too many particles are dispersed, due to a strong hydrodynamic interaction among particles, the particle shape after extension could deviate too much from the perfect spheroid. The dispersion was poured into a stainless pan of 90×110 mm with sidewalls and then dried on a flat table at the room condition. The depth of the mixture before drying was about 4 mm, and the average thickness of the film after drying was 250 μm. In Fig. 2, a typical variation in film thickness is shown. The film thickness varied approximately 15 μm (the standard deviation of the values shown in the figure). The dried film was flexible. Even when glycerin was not added, the dried film was flexible. This means that the dried film contains a certain amount of water and the glass transition temperature of the PVA film prepared in the research is below the room temperature. But the amount was not monitored. The usual drying time was about 36–48 h. Due to the evaporation of water, the viscosity of the film could not be measured at the operating (extension) temperature of 160 °C.

The film was extended by using a homemade extensional apparatus as shown in Fig. 3. The apparatus consists of eight jaws which hold the film, a jaw-moving mechanism, an oil bath, and a quench bath. The jaws can be moved radially with the same travel length by manually rotating a screw for a desired amount of extension, and therefore, the film can be extended biaxially at least inside the jaws. The homogeneity of the deformation will be discussed later. To extend the film, the film is softened by immersing the film-mounted jaws in the oil bath kept at 160 °C for 15 s first, and then, the softened film is stretched in the bath by turning the screw for extension by a desired magnitude. Just after the extension, the jaws holding the extended film are quickly immersed into the quench bath. Not to induce the retraction of extended particles, the time from the immersion bath to the quench bath was kept as short as possible.

The quenched film was washed with isopropanol first to remove the oil on the film. Then the film was dissolved in a water–isopropanol (30 %) mixture at 60 °C, and the dispersion of the deformed particles was spun in a centrifuge for faster sedimentation. The particles were collected by decanting the supernatant. The particles were washed five times with the water–isopropanol mixture by the same method, and then, the fluid that remained in the interstices was removed in a vacuum dessicator to collect liquid-free particles.

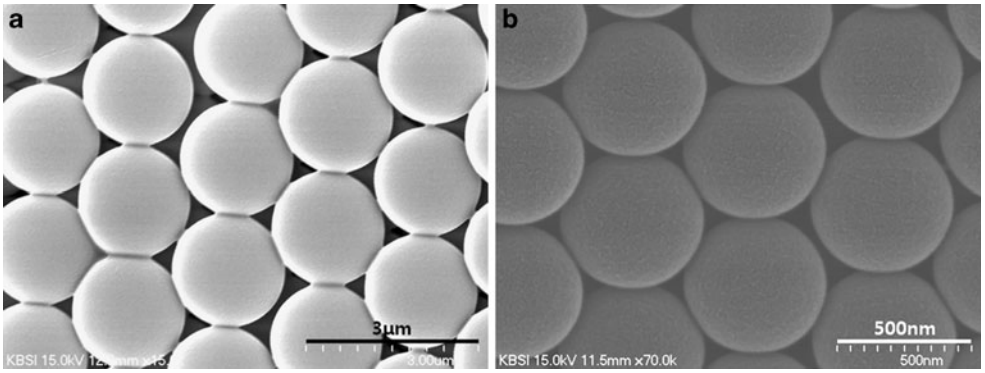

Fig. 1 SEM images of spherical PS particles before stretching: **a** 2.0 μm and **b** 520 nm

To confirm particle shape and measure the size of the particle, scanning electron microscopy was carried out (Hitachi S-4700). To prepare the specimen, a drop of the suspension with particles was spotted onto a silicon wafer and allowed to dry in the air. The Si wafer was sputtered with platinum before examination in the microscope. To capture the image viewed from the side, the sample holder was tilted by about 3–5°. For the elemental analysis, energy-dispersive X-ray spectroscopy (EDX) was used. Samples were placed on a carbon tape and coated by platinum for 60 s.

Results and discussion

Before investigating the deformation characteristics, the residual amount of PVA from PS particles was examined by EDX. For this purpose stretched particles with the aspect ratio of 8 were chosen. Since these particles are almost flat, there is a chance of layering of particles and hence washing should be very difficult compared with particles with smaller aspect ratios. When the stretched sample was first washed, residues were found in the SEM image, and oxygen was detected in the EDX analysis as shown in Fig. 4a. The oxygen should come from PVA. After washing five times, the SEM image showed distinct outlines of particles and the EDX detected no oxygen as shown in Fig. 4b. It is sure that the repeated washing effectively washed out PVA.

Figure 5a, b shows the typical shape of the particles collected from the central part of the film. If viewed from the side as shown in Fig. 5c, the particles are virtually exactly oblate spheroids without showing knife edges. This can be confirmed by comparing the outline of the particle with an ideal ellipse that is overlapped over the particle image. In the case of the particles shown in Fig. 5c, the longer and short axes are 2.58 and 1.52 μm, respectively. In this case the initial and final diameters (the distances between the diagonally located jaws) of the film are 60 and 70 mm. Hence if we assume that the deformation is uniform and affine all over the film inside the jaws, the longer axis and shorter axis are expected to be 2.52 and 1.59 μm. Therefore the deformation appears to be virtually

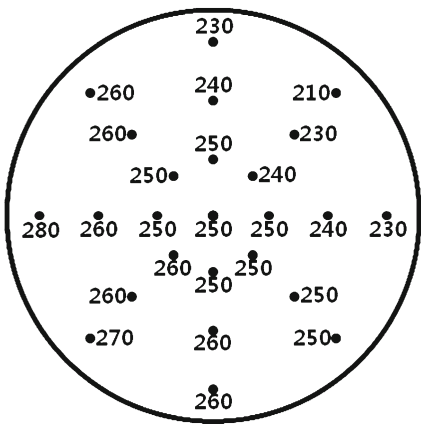

Fig. 2 A typical example of film thickness distribution (unit in micrometers)

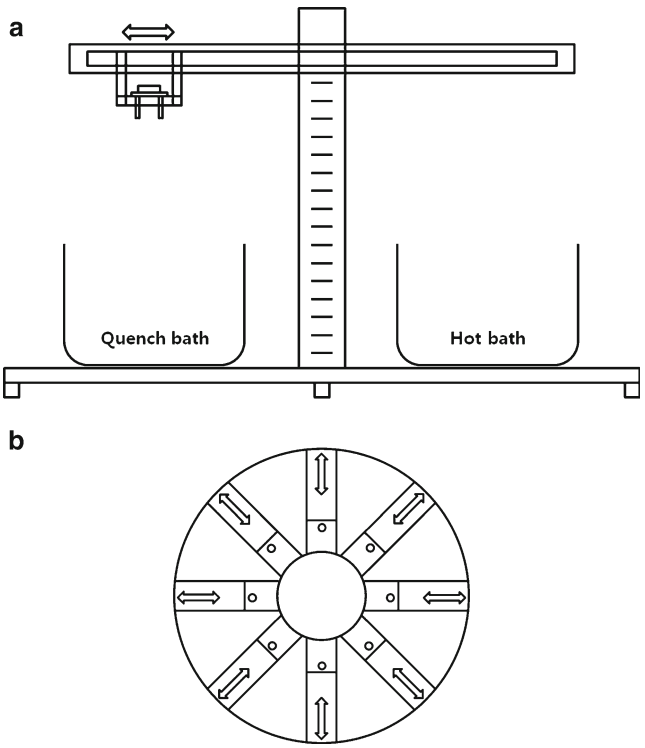

Fig. 3 **a** Schematic diagram of the experimental apparatus. **b** Film holder with eight jaws

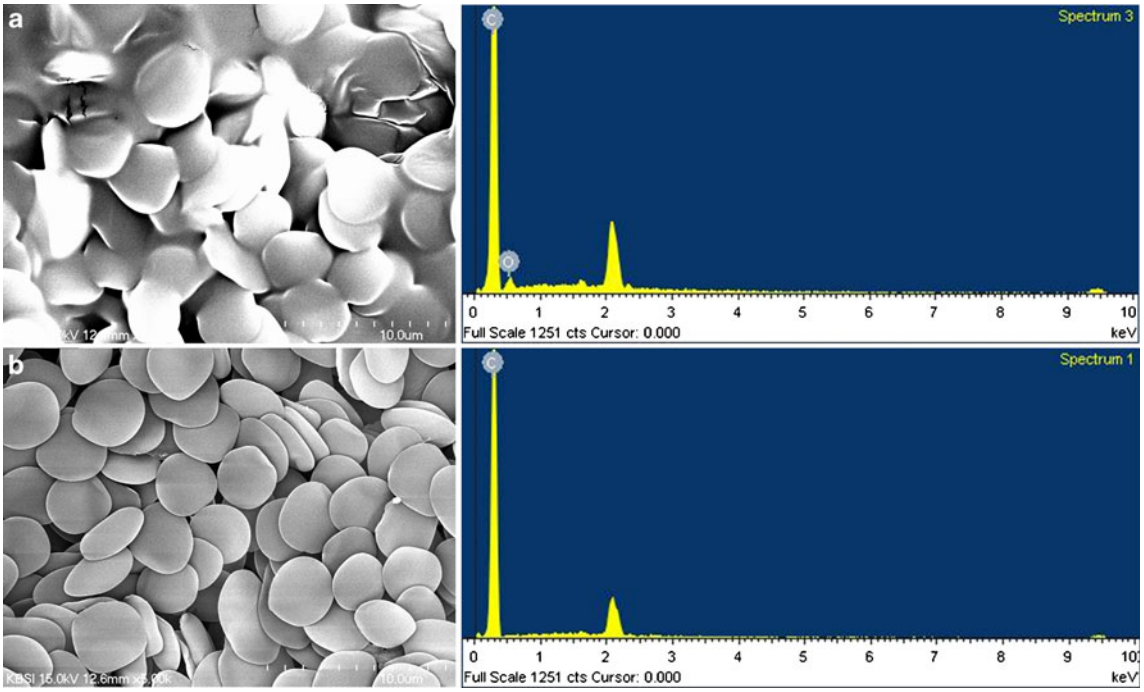

Fig. 4 SEM image and EDX result after **a** the first washing cycle showing oxygen at 0.55 keV (16.6 atomic% of oxygen) and **b** the fifth washing cycle showing no oxygen. The peak near 2.1 keV in the EDX result represents platinum used for coating

affine at least at the center. The shape of the particle is determined majorly by two factors in addition to the nominal biaxial strain imposed to the film: the effectiveness of deformation and retraction after deformation before quenched. The effectiveness of deformation can be guaranteed for a high extension temperature over the glass transition temperatures of PVA film and PS particle and a small interfacial tension between PS and PVA. Based on the fact that the extension temperature is at least 50 °C higher than the glass transition temperatures of PVA film and PS particle and the interfacial tension is as small as 3 $mN{\cdot}m^{-1}$ [21], it is surmised that the extension of PVA is virtually affine to the apparent deformation of the film. The driving force of the retraction is the force due to surface tension which scales as σ/a, and the retraction force is resisted by the viscous force which scales as $\eta\dot{\gamma}$. Therefore the proper time scale for the retraction should be $t_{\text{retract}} = \frac{1}{\dot{\gamma}} = \frac{\mu a}{\sigma}$. When the relevant parameter is used, it is found that t_{retract} has an order of 10^{-1} s. Therefore particles will become retracted to an extent while moving to the quench bath, and therefore, it is important to control this time lag to obtain particles of the predetermined aspect ratio. However the estimation of retraction time scale is based on the deformation of the PS drop in an inviscid fluid. So in the PVA environment, the time scale for retraction will be much longer than the value estimated here due to the resistance to deformation of PVA film itself. We checked the effect of the operating temperature of the oil bath by changing 20 °C, but the aspect ratio did not change with temperature. This means that the biaxial extension is not much affected by the change in viscosity ratio, and hence, the deformation closely follows the true biaxial extension.

To check the homogeneity of deformation of the entire film, small circles were drawn on the film before stretching

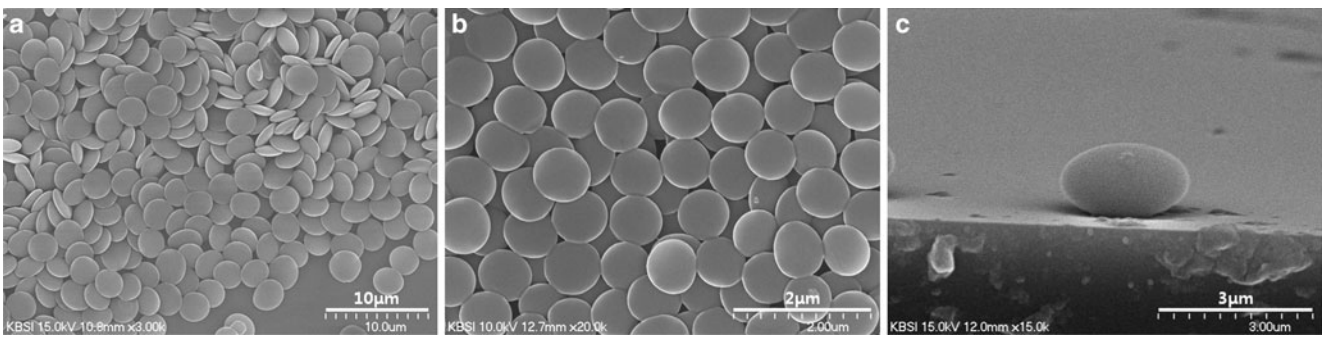

Fig. 5 Typical shapes of particles collected from the center of the film: **a** 2-μm particles and **b** 520-nm particles. **c** Side view of a stretched 2.15-μm particle

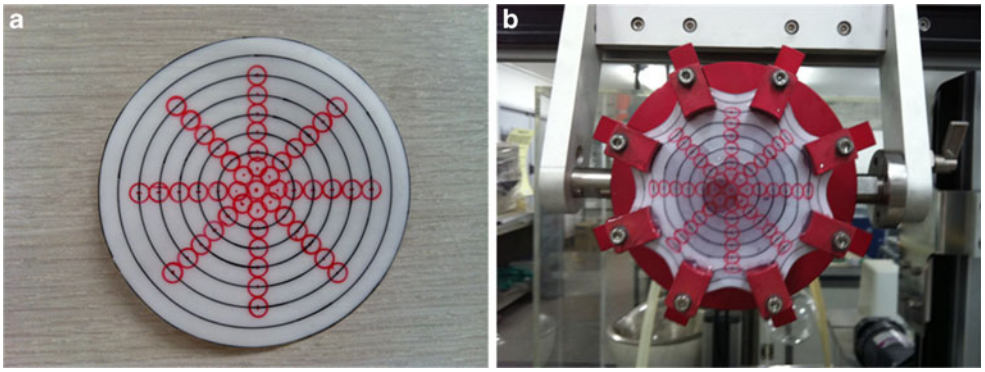

Fig. 6 Variations in local deformation **a** before stretching and **b** after stretching

and the shapes were compared before and after stretching as shown in Fig. 6. It is seen that the deformation is not uniform all over the film inside the jaws. Near the jaws a circle became an ellipse, which means that ellipsoids were produced at this region. Between the sides of jaws, there developed uniaxially elongational deformation so that prolate spheroids were produced. In Fig. 7 we have compared the shapes of particles generated at each region. To check the homogeneity of the deformation at the central part, concentric circles were drawn on the film before stretching and the aspect ratio of the particles from each ring was examined by collecting particles separately. The distance between neighboring circles was 6 mm before stretching, and sample numbers were given from the innermost circle to the outermost ring. In Fig. 8 we have plotted the aspect ratio of spheroids. Until the concentric ring 5, the particle aspect ratio remains almost the same for both cases of 520 nm and 2 μm. From this information it can be seen that only 25 % of the entire film was subjected to the true biaxial deformation and the number of spheroids obtained per one batch is 2.3×10^7 when the dried film thickness is 250 μm and particle loading before drying is 0.47 % before drying. To increase the number of particles, a thicker film can be used. In this case the drying time should be much longer than the present case. A larger particle loading can be used for higher productivity, but in this case, due to the stronger particle–particle interaction, particle shape could deviate too much from the spheroid. To increase the productivity, more than one film (five to six sheets of film) can be installed at a time between jaws. It is not expected that the blown film method can handle many layers of films at a time.

There should be minimum particle size that can be deformed by this method since the surface tension force resists to the imposed deformation. When a film that contains particles is extended, a biaxial stress should be applied to particles and the surface tension force resists to the deformation, i.e.,

$$\eta_{BE}\dot{\varepsilon} = \kappa\sigma = 2\sigma/a \tag{1}$$

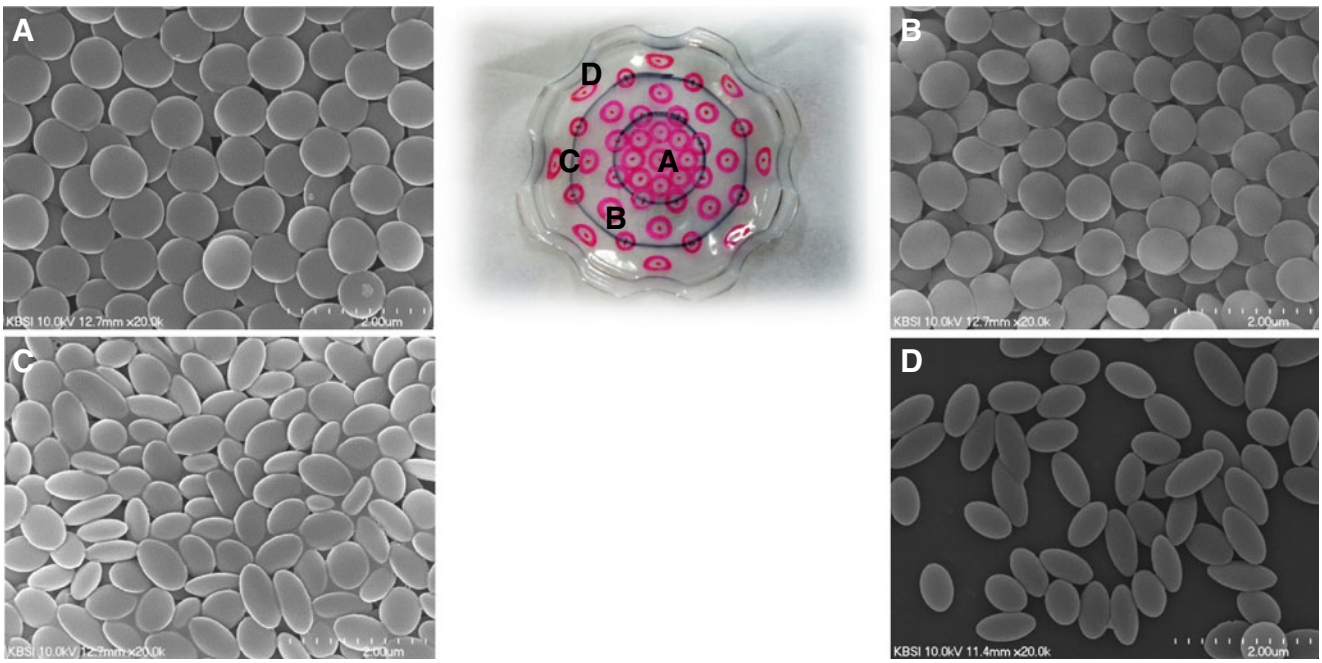

Fig. 7 Shapes of stretched particles from various positions

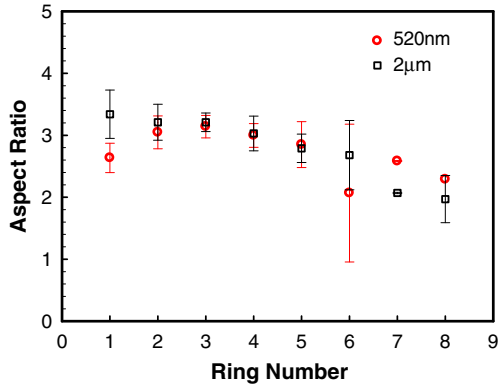

Fig. 8 Aspect ratios of particles collected from each ring for 2 μm and 520 nm particles

In the above equation, η_{BE} is the biaxial extension viscosity, $\dot{\varepsilon}$ is the extensional rate, κ is the total curvature, and σ is the interfacial tension. The extensional rate of the present experiment is estimated to be about 0.022 s^{-1}. Since the extensional rate is very small and the extensional deformation is not large, the PS melt will behave as a Newtonian fluid. Then $\eta_{BE}=6\eta_0$ [22], where η_0 is the zero shear viscosity. Since it was impossible to estimate the viscosity of the PVA film as described above, we infer the minimum level of imposed stress from the viscosity of PS. Since the viscosity of PS is dependent on molecular weight, we choose 160,000 Da (this value corresponds to the MW of 520 nm particles). At the working temperature of 160 °C, the zero shear viscosity of the PS is approximately 2.5×10^5 Pa·s and the interfacial tension is 3 $mN\cdot m^{-1}$. Then the minimum radius is estimated to be 200 nm from Eq. (1). It is a conservative estimate since the viscosity of PS is used rather than that of PVA film. The viscosity of PVA film should be larger than the viscosity of PS since we were able to extend it affinely as already described. Another important issue is the maximum attainable aspect ratio. As the deformation becomes large, the curvature at the edge becomes even larger. From the geometric reasoning, it can be shown that the curvature at the edge is $\frac{2k^6}{a}$, where k is the extensional deformation (final film diameter/initial film diameter). If k is 1.5 the curvature becomes 11.4 times the original value, which can hinder the deformation and induce fast retraction. Therefore submicron size particles with a large aspect ratio may not be obtained.

Conclusion

In the present study, we have shown experimentally that oblate spheroids can be generated by the biaxial extension of a polymer film containing spherical polymer particles. By holding the sample by eight jaws that move concurrently, a biaxial extension of a fine resolution could be imposed in a robust way. In addition to spheroids, ellipsoids and prolate spheroids could be also obtained.

Since there is no need to bend the film at the right angle to hold the film in the present case, the film thickness is not a problem as in the case of the blown film method. Therefore, even though the percent yield per batch appears to be higher with the blown film process since the film is held by a ring which does not seem to affect the deformation of the film, the total number of spheroids per batch will be much larger with the eight-jaw method used in the present research by using a thicker film. Also the present method is robust in that the deformation is always reproducible regardless of film thickness. We have confirmed that this method can be applied for particles with submicrons to 10 μm in diameter. Considering the thickness of the dried film, this method can be applied to particles of as large as 100 μm. In this case, however, a very concentrated PVA solution has to be used to prevent the sedimentation of particles before being dried.

In the present research, a practical and efficient method is present to produce oblate spheroids in a massive amount. The method reported here can be of help in fundamental researches such as rheology of suspension of nonspherical particles and the study on the electrophoresis of nonspherical particles. The deformed particles can be utilized in the study of particle shape effect in the areas including pharmaceutical science and inkjet printing. Especially they can be of great help in studying the microstructure formation and migration characteristics in colloidal suspensions while changing the dispersion characteristics.

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