Rapid Swelling and Pattern Formation in Hydrogel Particles

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We report on a novel wrinkle formation process of water absorbing hydrogel particles. When the hydrogel particles called Super Absorbent Polymer (SAP) are dropped onto water which is held in a cylindrical container, the particles rapidly swell at the air-water interface to form a sheet-like structure. Once the sheet-like structure reaches the wall of the container by its continuous in-plane expansion, it starts to buckle with a characteristic pattern of wrinkles. We applied a simple model to estimate the wavelength of the wrinkle, which was in agreement with experimental values. We also discussed the effect of buoyant force on the wrinkle formation.

Key Words: Super absorbent polymer / Gel particle / Swelling / Wrinkling / Buckling

1. INTRODUCTION

Super Absorbent Polymer (SAP) is a hydrogel particle which is made of cross-linked hydrophilic polymers. It retains a remarkable water-absorbing ability, i.e., it can swell rapidly up to 1000 times of its dry volume and can hold a large amount of water even when the compression stress is applied. For these reasons, SAP is widely used in various types of applications, such as baby diapers, feminine napkins, cosmetics, soil conditioners, building materials, drug delivery systems, etc.1-3)

Many efforts have been devoted to the synthesis of SAP to improve its water absorption and retention performances.3) Acrylic acid monomers and its sodium/potassium salts, and acrylamide monomers are most frequently used as commercial SAPs while some attempts have been done to use natural polymers.4) Polymerization and production methods have also been studied. Solution polymerization of monomers with a water-soluble cross-linker is frequently used. After gel-like elastic material of large volume is prepared, it is dried, pulverized and sieved to obtain a required particle size. On the other hand, the suspension polymerization technique is applied to obtain micro-beads (micro-spheres) with a given size in a direct manner.3)

Evaluation of prepared SAP has also been studied for years. Free-absorbency capacity, absorbency under load, swelling rate, ionic sensitivity and some other performances are tested to evaluate SAP performances in actual conditions.3)

Fundamental researches have also been conducted to understand physical mechanisms. Zhang and coworkers reported the volume transitions of SAP in physiological salt solutions.5) Budtova and coworkers studied deformation and solvent release behaviors of a single SAP particle under solvent flow.6) Meeker et al. conducted direct observations of slip and flow in pastes of micro-gels under shear flow.9) However, to the author’s knowledge, few studies have been reported on the dynamical behavior of SAP systems, i.e., the coupling between swelling and motions of many SAP particles and their transient properties as well.

In this paper, a dynamical process of the gel particles including swelling and motions is reported. As shown later, many SAP particles induce wrinkling of a sheet-like structure due to rapid swelling, which is different in behavior from previously-reported bulk gel systems.10-13)

2. EXPERIMENT

2.1 Gel Sample

In our experiments, dry hydrogel particles (poly(0.75 sodium acrylate-0.25 acrylic acid) cross-linked by N, N'-methylenebisacrylamide, commercial name: Aqua Keep® 10SH-NF, Sumitomo Seika, co. ltd., Japan)14) was used as received. Their average radii in dry/fully swollen states were about 25/150 μm respectively.6,7,14) Figure 1 shows the swollen gel particles. It is seen that they are almost spherical though each one is slightly deformed due to contact with neighboring particles.
2.2 Dropping Method
In each experiment, after the dry gel particles were held with a weighing paper having a fold, they were dropped onto the surface of distilled water (Millipore water, V = 200 ml) stored in a PMMA cylindrical container (diameter of the inner wall: 100 mm) by inclining the weighing paper by hand as fast as possible. This simple dropping method minimizes the difference in arrival time of the particles at the air-water interface and facilitates the (nearly) simultaneous start of swelling. A schematic of the experimental setup is shown in Figure 2.

2.3 Observation
Swelling behavior of the particles after dropping onto water was observed with 2 video cameras (VHX-200, Keyence, Japan) from the top and the side of the container. The frame rate was 30 images per second.

2.4 Measurement of Stress-Strain Curves
Shear Stress – Shear Strain curves for the hydrogel particles containing a given amount of water were measured with a rheometer (HAAKE MARS, Thermo Electron, Germany) in the double-cylinder geometry (material: PMMA, diameter of inner/outer cylinders: 35/55 mm respectively, height: 40 mm). Each sample was prepared by pouring water (Millipore water) into a given amount of dry particles with mixing as gently as possible, and held for more than a week inside a capped glass bottle. The appearance for all samples was paste-like. The rotation speed was 0.6 rpm (average shear rate: 0.14/s). In order to avoid undesirable wall slip of the gel particles, sand papers were adhered onto both walls. All measurements were done at room temperature and conducted 10 minutes after the gel particles were put into the double-cylinder.

3. RESULTS AND DISCUSSION
3.1 Swelling Behavior
Figure 3 shows the snapshots of the swelling behavior of the gel particles. In this experiment, the dry gel particle amount was 1 g or equivalently, the dry particle concentration was c = 1 g (particle)/200 g (water) = 0.5 wt%. As soon as the gel particles touch water (Figure 3(a)), they start to swell rapidly to form a sheet-like structure at the air-water interface (Figure 3(b)). Since other gel particles are supplied after the first arrival, the sheet-like structure continues to expand in the in-plane direction (Figure 3(c)). When the sheet-like structure covers the whole area of the interface, it then starts to buckle (Figure 3(d)). As further in-plane expansion of the sheet-like structure, it crumples and plunges into water (Figure 3(e), (f)). A few seconds after, the motion stopped and the wrinkle pattern ceased to change. In these pictures, “white” areas are seen. The white color corresponds to the dry powder of the gel particles, i.e., some particles do not participate in the wrinkling process but remain on the sheet-like structure without touching water. It is important to note here that the exact swelling behavior (for example, timing of wrinkling, position of the “white” spots, etc.) varied depending on how the particles were dropped onto water, while the typical features such as rapid swelling, formation of sheet-like structure, buckling behavior, and the wavelength of the patterns were unchanged. These dynamical processes are summarized schematically in Figure 4.

In order to characterize the wrinkling pattern, its wavelength was measured. The measurement was done manually by selecting 10 different points (where the wrinkles are clearly recognized) for each picture and then by measuring width of the wrinkles with a ruler. The values obtained were 3.7 ± 0.6, 4.2 ± 0.8, and 4.7 ± 0.9 mm for Figure 3(d), (e), (f).
respectively. It means that the wavelength increases with
time (though the increase stopped a few seconds after, as
noted above). The reason for this increase in the wavelength
might be considered as follows: as time passes, the sheet-like
structure (water surface) tends to recover its flatness because
the already swollen particles do not stay on the water surface
but plunge into water, which relaxes potential energy loss due
to variations in water height (refer to 3.3) and permits lower
order (larger wavelength) buckling.

3.2 Generation of Elasticity
As discussed in the previous section, the gel particles form a
sheet-like structure and then induce buckling. Here a question
arises: why and how the sheet-like structure is formed? The
key point is considered to be adhesion between particles.

In Figure 4, the shear stress-shear strain curves in the
double-cylinder geometry are shown for 3 different gel particle
concentrations. It is clearly seen that the initial slope (G =
300 Pa) is almost the same for the 3 curves while the yield
(maximum) stress is different, suggesting the existence of
the concentration-independent elastic regime at small strains.
The results are in contrast with ones reported by Borrega,¹⁵
where the elastic modulus of the suspension depends strongly
on its concentration. The reason for such difference is not
well understood, but might be explained as follows: in our
system, repulsion between particles due to dense packing⁹
is not present, i.e., total volume is not conserved as clearly seen
from its “white” appearance indicating the existence of voids.
Instead, adhesion gives rise to concentration-independent
elasticity. For the sample with c = 1 wt% (>25/150)⁹ = 0.005:
maximum concentration for the fully swollen gel), all water
is consumed to swell the particles and loose packing of the
particles with some voids provides elasticity. Even when the
concentration is decreased (c = 0.5 and 0.3 wt%), the particles

![Fig. 3. Snapshots of the swelling behavior from the top and the side of the container. The dry gel concentration was c = 0.5 wt%.
](image)

![Fig. 4. Schematic of dynamical processes.
](image)

![Fig. 5. Shear strain-Shear stress curves for c = 1.0 wt% (bold solid line), 0.5 wt% (thin solid line), and 0.3 wt% (dotted line).
](image)
become just fully swollen or a small amount of water remains outside the particles (but not too much for the particles to lose their contact). Thus the contact state of the particles does not change so much.

Based on these considerations, we assumed that elasticity in the sheet-like structure is also generated by adhesion between swollen gel particles on the water surface. Adhesion-induced elasticity in gel particle systems has not yet been directly confirmed, but might be verified by the tensile tests with in-situ observations. It is a topic for future study.

### 3.3 Estimation of Wavelength of Wrinkle

In order to estimate the wavelength of wrinkles, the shell buckling theory\(^3\)\(^,\)\(^16\) is introduced. The quasi-static state is assumed and the deformation of the sheet-like structure is described by the following equation.

\[
\frac{E H^3}{12(1-\nu^2)}\frac{d^4 u(r)}{dr^4} + T \frac{d^2 u(r)}{dr^2} + \Delta \rho g u(r) = 0, \tag{3.1}
\]

where \(E, H,\) and \(\nu\) are the Young’s modulus, thickness and Poisson’s ratio of the shell respectively, \(u(r)\) is the out-of-plane (vertical) displacement of the shell, \(T\) is the in-plane compression force (per unit length) acting on the edge of the shell, \(\Delta \rho\) is the density difference between water and environment (\(\Delta \rho = \rho_{\text{water}} - \rho_{\text{air}}\) in this case), and \(g\) is the gravitational constant (refer to Figure 4). The first, second and third terms express bending elasticity of the shell, in-plane compression, and energy loss due to variation in height of the water surface. Here the angular dependence is neglected for simplicity. Then the following solution is assumed.

\[
u(r) = \varepsilon \sin (kr), \tag{3.2}
\]

Substituting equation (3.2) into equation (3.1), we obtain the formula for the critical compression force above which the buckling starts to occur.

\[
T_c = \frac{E H^3}{12(1-\nu^2)} k^2 + \frac{\Delta \rho g}{k^2} \tag{3.3}
\]

By considering the boundary condition,

\[
k R = n \pi \quad (n = 1, 2, 3, \ldots), \tag{3.4}
\]

where \(R\) is the radius of the container, the critical force is re-written in the following manner.

\[
T_c = \frac{n^2 E H^3}{12(1-\nu^2) R^2} R^2 + \frac{\Delta \rho R^2}{\pi^2} \frac{1}{n^2}. \tag{3.5}
\]

For this moment, arbitrary \(n\) is possible. However, \(T_c\) it is physically determined so that the minimum is realized. This condition is satisfied by \(\frac{\partial T_c}{\partial n} = 0\) and we obtain the formula for the wavelength of the wrinkle,

\[
\lambda = \frac{2\pi}{k} = \left(\frac{4\pi^4 E}{3(1-\nu^2) \Delta \rho g H}\right)^{\frac{1}{2}}. \tag{3.6}
\]

Now let us estimate the wavelength by equation (3.6). In our experiment, \(E = 3G = 900 Pa\) (\(G\) is estimated as 300 Pa from the double-cylinder measurement), (assuming that the thickness of the sheet-like structure is given by the swollen particle size), \(\nu = 0.5, \Delta \rho = 1 \times 10^3 \text{ kg/m}^3,\) and \(g = 9.8 \text{ m/s}^2.\) The estimated wavelength becomes \(\lambda = 2.7 \text{ mm},\) which is smaller than the observed values (~4mm) but within the same order. This suggests that the buckling mechanism is explained by the compression of an elastic sheet made of a single (or a few at most) swollen particle layer(s) on the water surface.

### 3.4 Effect of Buoyant Force

According to Equation (3.6), the wavelength of the wrinkle can be controlled by some parameters in principle. In reality, however, change in parameters is not so easy as long as we use a single grade or type of SAP particles. For example, we first tried to change the wavelength through the change in \(E \text{ or } H\) by putting a large amount of salt into water (which was expected to change the swelling degree of the particles), but the resultant wavelength was almost the same. Then we tried to change the parameter \(\Delta \rho\) by putting liquid which is immiscible with water and smaller in density (stays between air and water). Among several candidates, we choose hexane (\(\rho = 650 \text{ kg/m}^3\)) in our experiment.

Figure 6 compares the wrinkling patterns (a) with and (b) without hexane on the water surface at \(t = 20\) sec. The

![Fig. 6. Wrinkling patterns for 2 different conditions at \(t = 20\) sec. (a) with and (b) without a hexane layer.](image_url)
observed wavelengths are (a) 9.1 ± 1.2mm and (b) 4.7 ± 0.9 mm respectively. On the other hand, our theoretical estimation gives 3.5 mm and 2.7 mm with/without hexane, where both the absolute values and the ratio underestimate the experimental ones. This result suggests that the wavelength can be controlled by an adjustment of the density difference and also supports the validity of equation (3.6) though it is still in a qualitative level.

4. CONCLUSION

In this paper, we studied rapid swelling behavior of gel particle systems and found a novel wrinkle formation process where swelling, motions as well as the adhesion between the particles play important roles. We applied a simple model to estimate the wavelength of the wrinkle, which was in agreement with experimental values. We added an additional liquid to study the effect of buoyant force on the wrinkle formation and successfully controlled the wavelength of the wrinkles.

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REFERENCES