Letter

Direct observation of swollen microgel particles by FF-TEM

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The morphology of water swellable microgel particles in its aqueous dispersion was studied by freeze-fracture transmittance electron microscope (FF-TEM) technique. The FF-TEM images showed the microgel particles were spherical shape and when its concentration was high, the soft gel particles were packed tightly with the deformation of their shape. The direct observation results support that the pseudo-plastic flow behavior of the semi-dilute microgel aqueous dispersion, namely, the apparent yield stress is likely to be due to the closed packing of the soft microgel particles.

Key words: Microgel, Morphology, Freeze-fracture TEM

I. INTRODUCTION

Water swellable microgels are useful as a viscosity thickening agent for an aqueous system such as cosmetics, paints, and foods. [1] Their thickening effect is strongly affected by their mechanical properties, size, and the size distribution.[2, 3] The authors have developed a novel inverse microemulsion polymerization system with a non-ionic surfactant, and the system gave water swellable microgels that can be used in cosmetic products. [4] The aqueous dispersions of the microgels show typical rheological properties like a colloid dispersion. In particular, the apparent yield stress appears when the volume fraction (ϕ) occupied by microgel particles exceeds over 0.84 ($\phi > 0.84$). [5] The result is conflicts with the classic colloid science concept. If the particles are hard-spheres, the yield stress should appear at around $\phi \sim 0.64$, namely, the random-closed-packing (RCP) limit. This study unveils the shape of the swollen microgel particles in an aqueous media by freeze-fracture transmittance electron microscope (FF-TEM) technique.

II. MATERIALS AND METHODS

The details of polymerization procedure for the water swellable microgels is described elsewhere.[3] The microgel is consisted of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), dimethylacrylamide (DMAA), and methylene-bis-acrylamide (MBA) as a crosslinker. The samples for FF-TEM observation were the aqueous dispersion of the microgel in various concentrations (0.14 ~ 0.4 g / dL). The freeze-fracture specimens were prepared as follows. The sample dispersion was quickly frozen in liquid nitrogen (- 220° C). Frozen specimens were broken off with a knife-edge under a low pressure atmosphere at low temperature, and the broken surface was irradiated carbon and platinum, resulting a thin layer on the surfaces. The replica imprinted the texture of the broken surface was put on a mesh grid for TEM observation. The replica was observed with

TEM system (H-7000, Hitachi, Tokyo, Japan).

III. RESULTS AND DISCUSSION

Fig.1 shows the morphology of swollen microgel particle at around crossover concentration (c*). The volume fraction (ϕ) occupied by the microgel particle in such concentration is estimated to be 0.4 according to Einstein's law. In this concentration, the microgel dispersion never shows the apparent yield stress, in other word, there was no elastic properties appear in such concentration. On the other hand, when ϕ was 0.84, the FF-TEM image substantially changed (Fig. 2). The surface of the replica was quite smooth and the particles closed packed each other with the deformation of their shape.

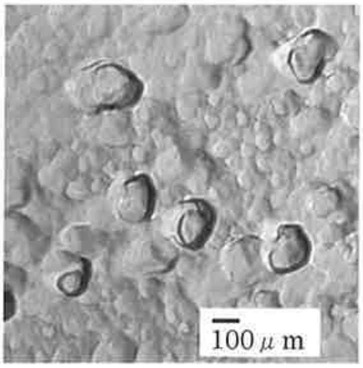

Fig. 1 The FF-TEM image of the swollen microgel particles (ϕ = 0.4)

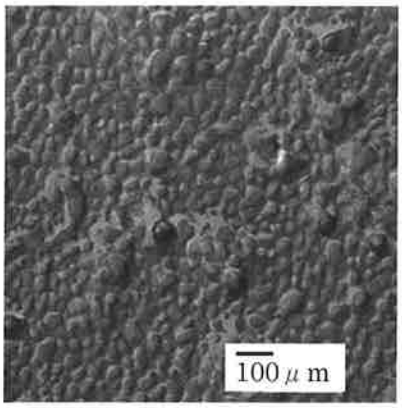

Fig.2 The FF-TEM image of the swollen microgel particles (ϕ = 0.9)

As described above, the microgel particles assumed to be dispersed as a spherical shaped particle from the relation between the intrinsic viscosities and concentrations according to Einstein's law in dilute regime.[3] However, the rheological properties of the microgel dispersion beyond semi-dilute regime deviate from the theory. If Einstein's law governs the rheological properties of the microgel dispersion, the elastic properties should appear at around the RCP limit, namely, ϕ ~ 0.64. However, the apparent yield stress appears beyond ϕ~0.84.[5] The reason of the controversial result was reveled from the direct observation of the swollen microgel particles in semi-dilute regime (Fig.2). Since the microgel was slightly crosslinked, 0.1 mol% crosslinker contained based on the total monomer, the microgel particles would be quite soft particles. Therefore, the microgel particles can deform and, in some case, deswollen, beyond theoretical RCP limit. The condensed microgel dispersion beyond the critical concentration exceeds ϕ ~ 0.84 shows gel-like behavior, namely, the soft microgel particles made space filling network structure. The direct observation of the swollen microgel also supports this discovery.

IV. CONCLUSION

The direct observation of microgel particles in swollen state has been succeeded by FF-TEM technique. The FF-TEM images could show a lot of information in respect of a swollen behavior of a microgel. In fact, some issues of the interpretation for the rheological properties of the microgels in previous reports have been revealed.

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