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Three Dimensional Joining of Thermoresponsive Particle-dispersed Gels †

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Abstract

Concentrated alumina suspensions were thermally gelled at room temperature using a triblock copolymer (PEO_{101}-PPO_{56}-PEO_{101}, Pluronic F127). The copolymer species assemble into micelles at temperatures above 15°C, yielding aqueous physical gel. The concentrated alumina aqueous suspensions were first prepared using the anionic dispersant of PAA, and then the copolymers were dissolved at a cooled temperature. The resulting suspensions were thickened at 30°C from low viscous state at 10°C. In particular, they were gelled when the copolymers were added at greater than 8mass%. The gels had large shear elastic modulus, and thereby the three dimensional periodic ceramic structures were successfully fabricated via a layer-by-layer joining of filamentary-excluded gel inks from a micronozzle. The copolymer-assisted concentrated ceramic gels may be useful for solid free forming.

KEY WORDS: (Solid free forming), (Colloid), (Gel joining), (Alumina), (Thermoresponsive polymer)

1. Introduction

Recently, solid free forming (SFF), which allows moldless manufacturing of ceramics, has received considerable attention[1,2]. Direct-ink-writing (DIW), one of these SFF methods, offers the ability to produce three dimensional periodic ceramic structures via a layer-by-layer deposition of filamentary-excluded gel inks from a micronozzle[3-5]. These structures may find widespread technological applications such as sensors, composites, and tissue engineering scaffolds[4].

Physical particle gels which rely on the formation of a physical bond between the particles in concentrated suspensions have been prepared for the DIW technique [5,6]. They exhibited a well-controlled viscoelastic response, i.e., they flow through the deposition nozzle and then set immediately to facilitate shape retention of the deposited features[4]. These characteristics have been achieved with careful control of colloidal forces to first generate a highly concentrated, stable dispersion, followed by inducing system change (e.g., ΔpH, salt concentration or solvency quality) for destabilization that promotes three dimensional physical bonding of suspended particles[6]. Practically, such changes are performed by adding and mixing acid, base, or salt. However, the simultaneous mixing and gelling may result in large inhomogeneities[1] that may block the nozzles. A better approach may be to use a reaction that promotes system change in situ.

Nonionic macromolecular surfactants of triblock copolymers of poly(ethylene oxide)-poly(propylene oxide)- poly(ethylene oxide), often denoted PEO -PPO-PEO copolymers have been known to be thickening or gelling agents on heating[7]. In case of PEO_{101}-PPO_{56}-PEO_{101} (Pluronic F127, BASF), the copolymer species assemble into micelles at temperatures above 15°C, yielding a physical gel when the copolymer concentration exceeds ~20% (against mass of water solvent)[8]. This is completely reversible, i.e., the viscous fluid reforms when the gel cools to temperature below 15°C. Nevertheless, as far as we know, less attention has been paid to the copolymer as a reversible gelling agent for ceramic colloidal processing.

Recently, we have demonstrated that that the alumina suspensions with the copolymer were thermally gelled and exhibited a good viscoelastic response for ceramic SFF[9]. We have also clarified the influence of poly(acrylic acid) (PAA) concentration on the gelling behavior[10]. An anionic surfactant of PAA is extensively used as a dispersant for preparing concentrated suspensions of ceramic oxides[11]. In this study, the influence of the copolymer concentration on the gelling behavior was investigated.

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2. Experimental

Materials. Alumina (TM-DAR, Taimei Chemical, Japan) was used as the model ceramic powder. The specific surface area of the powder, measured by BET method, was approximately 14.5m^2/g, yielding an equivalent spherical diameter of ~100nm. Ammonium poly (acryl acid) (PAA-NH$_4$) (D305, MW~8,000, Chukyo yushi, Japan) was used as dispersant. PEO$_{101}$-PPO$_{56}$-PEO$_{101}$ tri-block copolymer (Pluronic F127, MW~12,000, BASF, Germany) were used as gelling agent.

Preparation of alumina suspensions. The alumina powder was mixed with the deionized water containing PAA-NH$_4$ by ball-milling for 24h. The solid volume fraction of alumina in aqueous solvent was set to be 35vol%. The amount of PAA-NH$_4$ added was 0.4mass% relative to powder. Then, the copolymers (6, 8 and 10mass% relative to powder) were added into the as-prepared alumina suspensions under agitation at cooled temperature below 10°C. The resulting suspensions were treated by a planetary mixer to be mixed homogeneously and to remove bubbles.

Rheological Measurements. The rheological measurements of the colloidal inks were conducted using HAAKE Rheostress RS600 (Thermo fisher scientific Inc., USA). As sensor attachments, cone-plate type sensors (diameter=20, 35mm, angle=1deg.) were employed. For measurement of flow curves (shear stress or apparent viscosity versus shear rate), samples were homogenized by shearing at an identical rate of 20s^{-1} for 10s and left standing for an additional 10s prior to measurement to avoid undesired influence from different mechanical histories. In the steady-state measurement, the shear rate increased logarithmically from 0.1s^{-1} to 100s^{-1}, over the time period of 2min. The suspension temperature was controlled to be 10 or 30°C. In dynamic measurements, an oscillatory shear stress was applied with amplitude in the range 10^1-10^4 Pa at a constant frequency of 1 Hz. The elastic or storage modulus (G') in the viscoelastic linear region with the shear stress amplitude was evaluated.

Solid Free Forming. Three dimensional periodic colloidal structures were fabricated using a robotic deposition apparatus (SHOT mini-200α, Musashi Engineering, Japan). The three-axis motion of the x-y and z-stage was independently controlled. For the deposition, the alumina suspension was housed in a syringe and deposited through a tapered stainless steel nozzle at a volumetric flow rate of 3mm/s. A constant pressure was applied to induce the gel flow through the nozzle. The deposition process was carried out in air.

3. Results and discussion

In this study, the aqueous alumina suspensions were prepared with PAA concentration of 0.4 mass%. Then, three different amounts of the copolymer (6, 8, and 10 mass%) were added. The resulting suspensions exhibited good fluidity at 10°C in our eye inspection. **Figure 1** shows the flow curves of these suspensions at 10°C. As can be seen, no significant difference was observed on their flow curves, indicating that colloidal stability was not significantly affected with the present amounts of the copolymers. At the cooled temperature (10°C), the copolymer does not form micelle, existing as unimer$^{12)}$.

When the suspension temperature was heated to be 30°C from 10°C, these suspensions were thickened in our eye inspection. **Figure 2** shows the flow curves of the suspensions at 30°C. As can be seen, the shear stress and the apparent viscosity enhanced, compared to the results shown in Fig.1. They increased with the copolymer concentration, and the suspensions showed a typical shear thinning behavior above the yield stress. The gelling was observed for the suspension with the copolymer concentrations of 8 and 10 mass%. This gelling behavior was obviously attributed to the thermally-induced micelle formation of the copolymer. When stressed beyond its yield point, a colloidal gel exhibits shear thinning flow behavior due to the attrition of physically bonded networks formed in the entire suspension. The yield stress increased with the copolymer concentration.

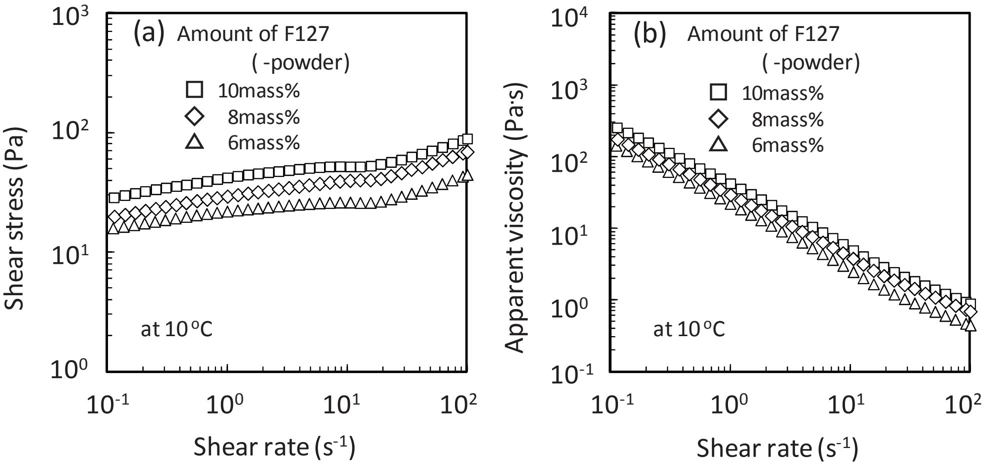

Fig.1. Flow curves of 35vol% alumina suspensions at 10°C.
(a) shear stress as a function of shear rate. (b) apparent viscosity as a function of shear rate.

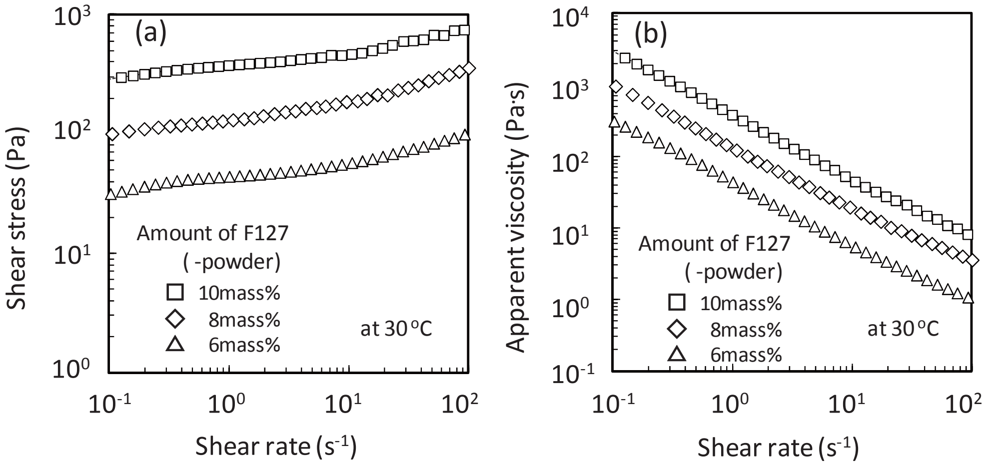

Fig.2. Flow curves of 35vol% alumina suspensions at 30°C.
(a) shear stress as a function of shear rate. (b) apparent viscosity as a function of shear rate.

Figure 3 shows the relationship between the shear elastic modulus and shear stress of the concentrated alumina suspensions induced at 30°C, as a function of the copolymer concentration. The shear elastic modulus was determined as a function of the shear stress amplitude. For the gelled suspensions (copolymer concentration=8 and 10mass%), a pseudoplateau was obtained at low shear stress amplitude. This region corresponds to the vicsoelastic linear region, in which the internal structure of the suspensions is not disrupted upon shear application (gel state). Then, for shear stress amplitudes larger than a critical value, a strong decrease in the shear elastic modulus takes place, which corresponds to a nonlinear viscoelastic response of the system. For 8 and 10 mass% of the copolymer concentration, the values pertaining to the vicsoelastic linear region were ~8,800 and ~2,500Pa, respectively. A minimum elastic modulus of ~2,000Pa is required for the colloidal gel when applied to the DIW method for producing complex three dimensional structures[13]. These gels satisfied this condition. On the other hand, the pseudoplateau region was not observed for the suspension with 6 mass% of the copolymer concentration, indicating that the suspension did not transform to a gel state.

In this study, the copolymer was used as gelling agent. It has been reported that gelling of the copolymer solution is due to the packing of spherical micelles of the copolymer as the micelle concentration approaches the critical volume fraction of 0.53 [14]. In the copolymer concentrations of 8 and 10 mass%, the copolymer species would assemble into micelles at temperatures above 15°C and the micelle concentration would approach the critical volume fraction at ~30°C. In fact, only copolymer-dissolved aqueous solutions became a stiff gel at 30°C for those copolymer concentrations. On the other hand, it did not gel at 6 mass%, indicating that the micelle concentration would be much less than the critical value.

The PAA-stabilized alumina suspension containing F127 copolymer was easily housed in a syringe at 5°C, because it was in fluidic suspension at temperatures <10°C. Then, the suspension was warmed at 30°C to be gelled. Because of a relatively good colloidal stability, it transformed to a gel state homogeneously. The thermally induced gel flowed through the nozzle with a constant deposition speed of 3mm/s. As the gel exits, it formed a rod-like filament with a rigid core-fluid shell architecture which allows the rods to fuse together at their contact points[4]. A shown in **Fig. 4**, we have fabricated the three dimensional lattices of alumina colloidal gel using the DIW technique. The present layer by layer deposition of the extruded gel was carried out in air. A significant clogging problem was not observed, indicating that F127 copolymer may act as a humefactant as well.

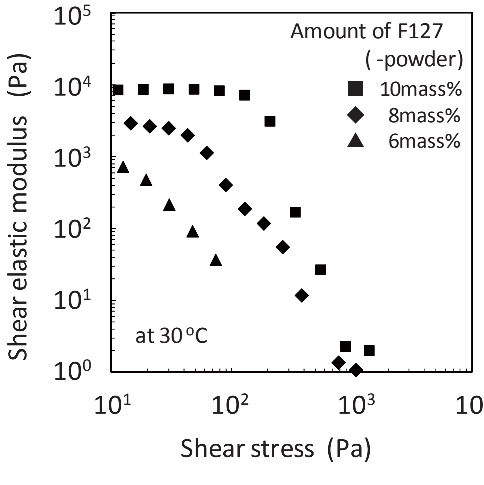

Fig.3. Shear elastic modulus as a function of shear stress for the alumina gels induced at 30°C.

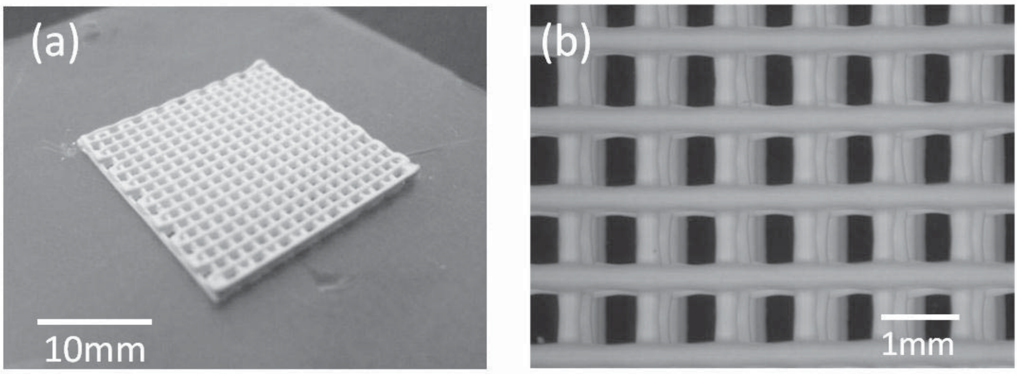

Fig.4. Optical images of the three dimensional periodic structure of alumina gel fabricated in this study. (a) external view. (b) magnified view

4. Conclusions

In this study, the PAA-stabilized alumina (ϕ= 35vol%) suspensions were thermally gelled using the triblock copolymer. The thermally induced gels had excellent viscoelastic properties with the present F127 concentrations. It was also demonstrated that the three-dimensional periodic structures were directly fabricated using the copolymer-assisted alumina gels. The present thermoresponsive ceramic suspensions may be useful for advanced ceramic colloidal processing.

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