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Ceramic Nanoparticle Ink for Direct Colloidal Assembly[†]

KONDO Akira*, ABE Hiroya** and NAITO Makio***

Abstract

Y₂O₃ stabilized ZrO₂ (YSZ) whose equivalent spherical diameter was 77nm was used as nanoparticles, and YSZ/ethanol colloidal dispersion with a volume fraction of 30vol% was prepared using poly(ethylenimine) (PEI) as dispersant. Then, colloidal gelation was induced by adding a small amount of nonadsorbed polymer, poly(vinyl butyral) (PVB) into the colloidal dispersion. The yield stress of the colloidal dispersion increased remarkably when PVB was added at 1mass%-powder or more. The two dimensional colloidal patterns of YSZ were directly formed by extruding the colloidal gel through a micro-nozzle.

KEY WORDS: (direct ink writing), (colloidal gel), (viscoelastic), (nanoparticles)

1. Introduction

Direct writing techniques offer the ability to produce ceramic components on-demand with complex structures. These techniques can be attractive routes for advanced ceramics, sensors, composites, tissue engineering scaffolds and photonic materials^{1,2}. Several approaches such as robocasting^{3,4}, fused deposition^{2,5}, and micropen writing⁶ have been introduced and have demonstrated solid freeforming of 2D and 3D colloidal structures via a layer-by-layer deposition of particle based inks. In each approach, ink is continuously extruded through a micro-nozzle to create a filamentary element.

Nanoparticle suspensions for the filament-based direct writing technique must satisfy two important criteria⁴. First, they should exhibit 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. Secondly, they should contain a high volume fraction of powder to minimize drying-induced shrinkage after assembly is complete, i.e., the particles network must be able to resist compressive stresses arising from capillary tension. The developed nanoparticle ink was an aqueous colloidal gel comprised of poly(acrylic acid)(PAA)-coated BaTiO₃ nanoparticles, whose interactions were carefully modulated by changing ionic strength through the addition of monovalent or divalent salt species⁷.

Here, we report nanoparticle dispersed colloidal gels with ethanol solvent for the filament-based direct writing. In this study, the colloidal gelation was successfully induced by adding small amount of nonadsorbed polymer into the colloidal sol.

2. Experimental

Materials. Y₂O₃ stabilized ZrO₂ (YSZ) powders (TZ-8Y, Tosoh, Japan) were used as model particles. The specific surface area of the powder, measured by nitrogen adsorption, was approximately 13.2m²/g yielding an equivalent spherical diameter of 77nm. Branched poly(ethylenimine) (PEI, MW~10,000, Nippon Shokubai, Japan) was used as dispersant. PEI has been proved to be a good dispersant of nanosized ZrO₂ in aqueous systems⁸. A high affinity of PEI on oxide surfaces can also promote the colloidal stabilization of oxide particles in an ethanol system⁹. Poly(vinyl butyral) (PVB, #3000K, Denka, Japan) was composed of 81mol% vinyl butyral, 12mol% vinyl hydroxyl, and 7mol% vinyl acetate units, and the number average of their polymerization is ~800. Ethanol (purity 99.5%, Wako Pure Chemical, Japan) was used as solvent.

Preparation of Colloidal Gel. The solid volume fraction of YSZ in the ethanol suspension was set at 30vol%. The amount of PEI added was 1.5mass% of the solid. The suspension was milled in a laboratory scale ball mill for 24h using ZrO₂ milling media. Then, PVB was mixed using a conventional stirrer for the fluid-to-gel transition. The total amount of PVB added was 0.01, 0.1, 1 and 3mass% of the solid.

Rheological Measurements. The rheological measurements of the colloidal inks were conducted using a rheology meter (HAAKE Rheostress RS600, Thermo fisher scientific Inc., USA). As sensor attachments, cone-plate type sensors with 20 and 35mm diameters were employed. To avoid undesired influence from different mechanical histories, samples were

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homogenized by shearing at an identical rate of 20s^{-1} for 10s and left standing for an additional 10s prior to measurement. Flow curves were automatically recorded via a built-in program. The measurements were performed with the following input conditions: the shear rate increased logarithmically from 0.1s^{-1} to 100s^{-1} , over the time period of 2min. The measurement temperature was 25°C .

Direct Ink Writing. A robocasting system with a micro-pen was employed. The ink of the resultant colloidal gel was housed in a syringe and pushed out as a filament through a tapered nozzle (diameter, $D=200\mu\text{m}$) by a pneumatic system. The filament was deposited on a plate while the position of the nozzle was moving with a CAD system control. The deposition was carried out at 25°C in air.

3. Results and Discussion

Figures 1 and 2 show apparent viscosity and shear stress as a function of shear rate for the prepared colloidal inks with various contents of PVB. Each colloidal ink displayed shear thinning behavior with yield stress. In Fig. 2, the flow curves are fitted with the Herschel-Bulkley model¹⁾, as described by :

$$\tau = \tau_y + K (G_p)^n \quad (1)$$

where G_p is the shear rate, τ is the shear stress, τ_y is the yield stress, n is the shear thinning exponent and K is the viscosity parameter.

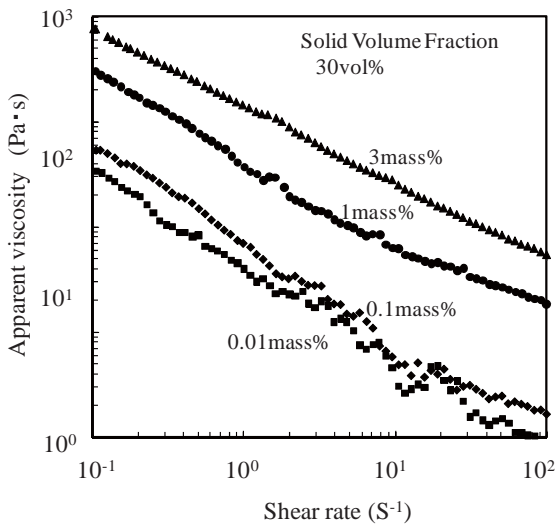


Fig. 1 Apparent viscosity as a function of shear rate for the prepared colloidal inks

Yield stress is the shear stress at vanishing shear rate. It represents the minimum stress leading to deformation of the static form of the material. Here, we determined the values of yield stress from the fitting curves of the Herschel-Bulkley model. Figure 3 shows the relationship between the yield stress and PVB added. The yield stress at 3mass% was about 70Pa which was enough to be applicable to the direct writing technique. On the other hand, the yield stress of the suspension without PVB was less than 1Pa. The addition of PVB promoted flocculation well, suggesting increasing interparticle attractive forces.

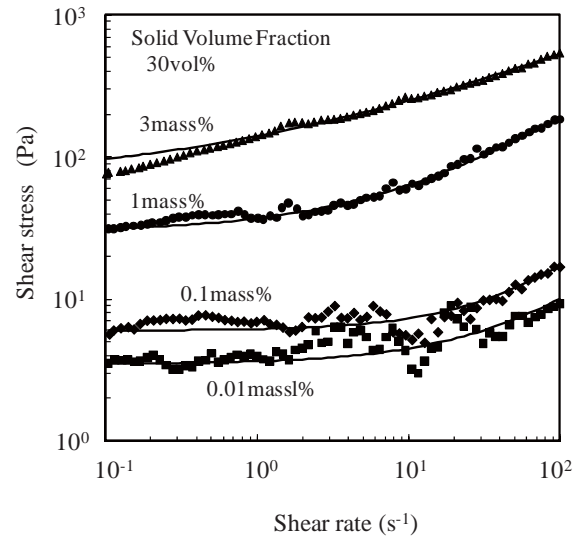


Fig. 2 Shear stress as a function of shear rate for the prepared colloidal inks

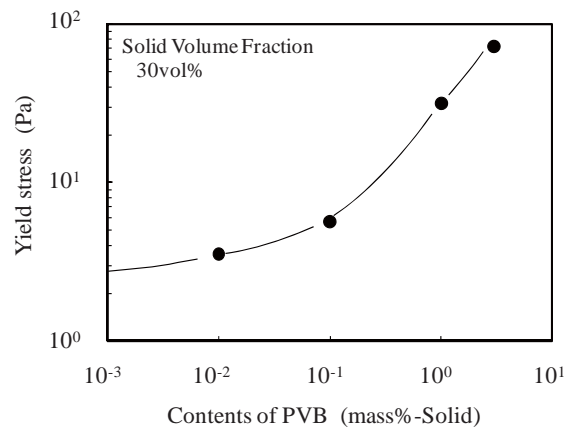


Fig. 3 Relationship between the yield stress and PVB content

In this study, it was found that the small amount of PVB added induced strong flocculation, giving to fluid-to-gel transition. PVB with this amount does not have gelling ability. In fact, the solvent viscosity with dissolved PVB of 3mass% was negligibly small compared to those of the suspensions. In the suspension, PEI was fully coated on YSZ nanoparticles, whereas PVB existed as nonadsorbed polymer. It was noted that the phenomenon was not observed when the volume fraction of YSZ was less than 30vol%, suggesting that it would be probably explained by depletion interaction¹⁰. The detail of the mechanism will be discussed in a separate paper.

As shown in **Fig. 4**, various patterns of 2D structures assembled with YSZ nanoparticles were successfully obtained by direct-writing with the PVB added colloidal gel.

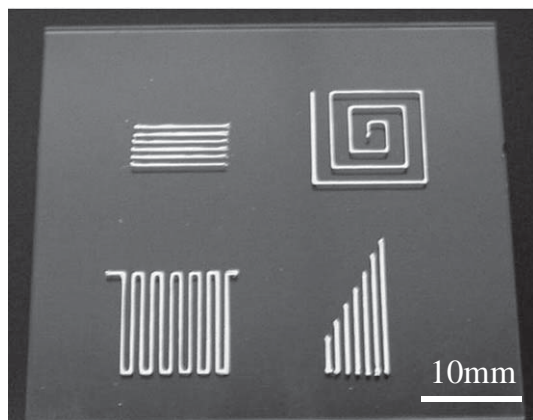


Fig. 4 Photograph of various 2D patterns by direct-writing

Conclusions

In this study, we propose an approach to producing nanoparticle colloidal gel for a direct writing technique. Salt species which are used in aqueous systems were not employed. Instead, we used PVB polymer as a gelation agent. Using the present colloidal gel, 2D patterns of YSZ nanoparticles were directly formed.

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