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Three Dimensional Inkjet Fabrication of Nano-Composite Hydrogel

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Abstract

We have developed the direct inkjet 3D fabrication system which can vary mechanical strength of nano-composite hydrogels on demand. The object body contains various parts which have gradual strength, colors and other physical properties. In addition, over-hanging and hollow structures were successfully obtained by using support material. It can be said that the hydrogel 3D fabrication system is able to construct a fine objects having partially controlled mechanical strength. Those objects have a potential of adding a unique value into the medical 3D model, and other applications.

The methodology of hydrogel fabrication and the properties of the hydrogel object are discussed, and the blood vessel model and the hollow vascular model were prepared for surgical training application.

Introduction

In an additive manufacturing and a rapid modelling industry, a lot of unique applications are proposed. [1] In this field, there is still room for new material improvement to create a novel applications. Although soft materials, such as rubber-like material and elastomers are commercially available, [2] more flexible material is keenly required in medical and healthcare fields. Such kind of soft material expected to be used as a part of human organ model, an artificial limb, and artificial blood vessel etc.

Hydrogel is an attractive material in fundamental and practical point of view. [3] Because of high content of water, their texture and other physical properties are quite similar to human body or organs. In addition, they have extensively studied because of their environmental sensitivity. [4]

In the last decade, several types of tough hydrogel are proposed, such as, topological (TP) gel, nanocomposite (NC) gel, Tetra PEG gel, double network (DN) gel. Above all, NC gel [5] is known as quite flexible and tough compared to generally known fragile hydrogels. However, the precursor liquid of NC gel is reported to be fundamentally unstable and not easy to handle as a liquid because of the thixotropic property. [5]

Recently, the inkjet digital printing technique has been extended from 2D printing into 3D fabrication. The inkjet technique is mainly applied into direct material jetting method and the powder-based binder jetting method. In the direct material-jetting method, liquids are applied onto the table from the inkjet heads, then cured by UV light, and those processes are repeated layer-by-layer. The key advantages of inkjet technique are the multiplicity of materials and the precision of patterning especially in material-jetting method.

T. Jungst et al. summarized the 3D printable hydrogels in their review paper. [6] They concluded that the 3D hydrogel printing should be one of a key technology of the biofabrication in tissue engineering applications.

To date, a precise 3D fabrication of those hydrogels is not realized. In this study, we focus on the 3D fabrication of NC gel applying inkjet 3D printing technique based on material-jetting method.

NC gel contains disk-like inorganic clay which have typical dipolar structure. The dipolar clay causes the instability and the thixotropic manner mentioned above. Using the appropriate dispersant to the clay, the viscosities of the NC gel precursor liquid became sufficiently below to eject from the nozzle of an inkjet head. We investigated a tough, dry-resistant hydrogel composition and the removable support materials.

Also, we have developed the inkjet 3D fabrication system which can vary the strength of hydrogel on demand. With this method, the 3D structure hydrogel object body contains various parts which have gradual strength, colors and other physical properties. We may say that those hydrogel 3D fabrication technique could add a unique value into the medical 3D model, and other applications.

In this paper, the methodology of hydrogel fabrication and the properties of the hydrogel object are discussed and medical applications were shown.

Nanocomposite Gel (NC Gel)

Figure 1 depicts a typical structures of NC gel. Based on various analytical studies (transmission electron microscopy, thermogravimetry, X-ray diffraction (XRD), differential-scanning calorimetry, Fourier-transform infrared spectroscopy for dried NC gels; dynamic light scattering and small-angle neutron scattering (SANS) for NC gels), Haraguchi et al. concluded that the structure of NC gel is the multiple crosslinking of the disk-like inorganic clays and water-soluble polymers. [5] The surface of clay has a lot of hydrogen bonding site and the amide-side group on the polymer chain. Because of the highly uniform clay dispersion and the strong interaction between flexible polymer chains and inorganic clays, NC gel shows outstanding mechanical and optical properties. Those properties can be variable over the wide range by controlling the concentration of components.

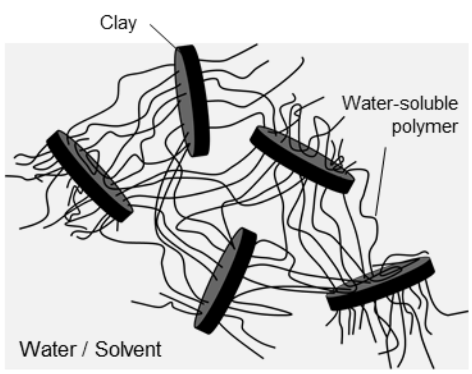


Fig. 1 *A schematic representation of NC gel structure.*

Haraguchi and Takada investigated the *in-situ* synthesis of NC gel with the stimulation of UV irradiation. [7] Figure 2(a) to (c) shows the propagation of the in situ free radical reaction. Photo initiators are thought to be surrounding inorganic clays (a), and the UV irradiation produces free radicals from photo initiators. Polymerization is mainly began from the surface of the clay (b). Finally, clays and polymers make a strong network in water solution (c).

Combining the volumetric control by using the inkjet digital printing method and the in situ synthesis by photo irradiation method, it is expected that a highly precise NC gel three dimensional objects could be obtained.

Experimental

Ink preparation

1st ink: NC gel precursor Synthetic inorganic clay was dispersed in water solution. The clay has a typical dipolar structure. The anionic dispersant was applied and the stability of dispersion is improved significantly. Accordingly, uniform water solutions containing clay, solvent, monomer, photo initiator, and surfactant were prepared.

2nd ink: Diluent The second ink is used to dilute the first ink on the deposited surface.

3rd ink: Support material The third ink is used to form a support structure.

Data construction

The data to fabricate were created with the following scheme 1 through 4.

1. Model part (NC gel structure) data are drawn by using 3D CAD (Fig. 4(a)).
2. Support part data are also defined as supporting over-hanging structures (Fig. 4(b)).
3. Both data are converted into STL format files.
4. STL files are converted into slice data as two-dimensional images.

Apparatus and process

Figure 3 shows the schematic view of the inkjet direct printing and UV curing apparatus. At least three inkjet heads were used for patterning objects. We utilized the inkjet head, MH2420 (Ricoh Co. Ltd.). While the table is moving, the first head deposits the precursor of NC gel which is illustrated in Fig. 2(a). The second one deposits the diluent ink. The droplets are united onto the layer at the specified proportion and mixed to form the discrete volume element. The third head deposits a support material. A support material is essential for making an overhang shape, such as the inside and the downside of the tubular shape in Figure 4(b). Afterward, UV light is irradiated on top of the layer, and the above mentioned processes are repeated layer by layer.

As shown in Figure 4(c), the printed objects are coexisting with support part. Finally, we obtained objects after the support materials are removed after printing process (Fig. 4(d)).

Measurement

The compression behavior of printed objects are measured by Autograph (AG-I, Shimazu Co. Ltd.) with 5kN load cell at the speed of 5mm/min. The compression modulus is analyzed at 0% to 10% strain range.

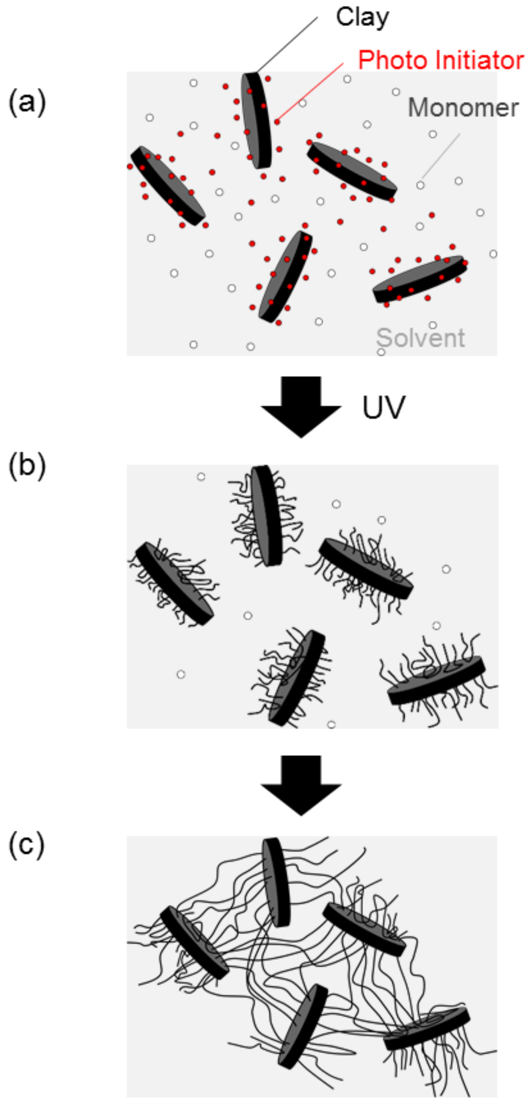


Fig. 2 *A schematic representation of in-situ synthesis of NC gel; (a) NC gel precursor including inorganic clays and monomers, (b) A propagation of polymer from the surface of clays, (c) in situ synthesized nanocomposite gel.*

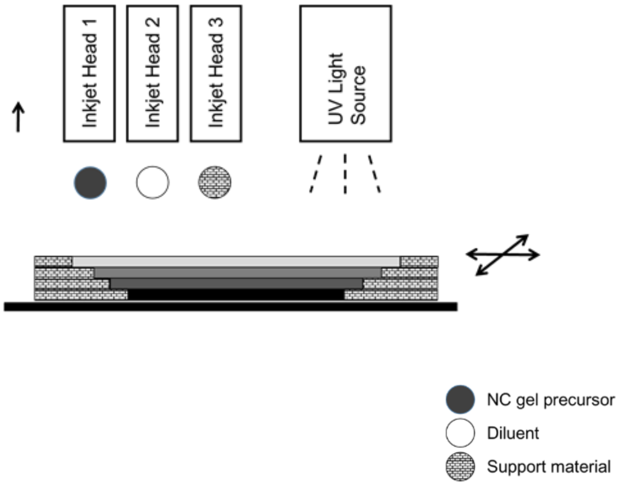


***Fig. 3** A schematic representation of apparatus. While the table is move to X and Y direction, inkjet heads and the UV light source move up to Z direction.*

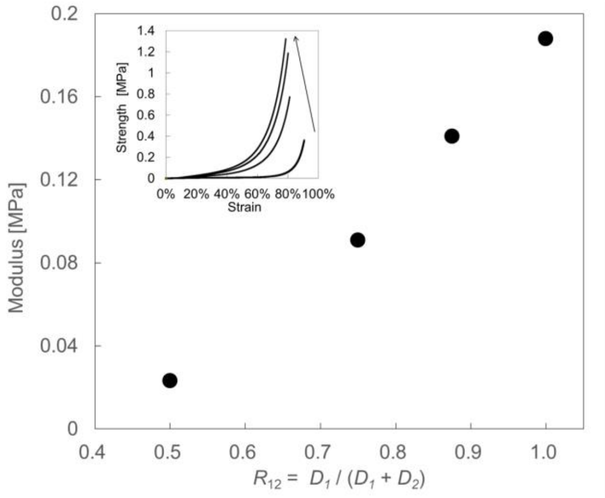


***Fig. 5** The compression behavior and the compression modulus of specimens varied the ratio of the first and the second ink.*

Results and Discussion

To confirm the variability of the mechanical property by controlling the concentration of polymers and clays, we have made specimens by varying the ratio of the first ink of NC gel precursor and the second ink as diluent by controlling the proportion of the first ink droplets and the second one in the same volumetric element. The ratio (R_{12}) of the first ink (D_1) and the second ink (D_2) is defined as equation 1.

$$R_{12} = \frac{D_1}{D_1 + D_2} \tag{1}$$

The ratio is controlled to become 0.5, 0.75, 0.875, and 1.0. Figure 5 shows the compression behavior and the compression modulus of each specimen ranging from 0.02MPa to 0.2MPa.

The compression modulus is found to be proportional to the ratio of the first and the second ink. This result indicate that the crosslinking density of NC gel is spatially controlled, and the above mentioned direct inkjet 3D fabrication method is able to vary the mechanical properties at each volumetric element.

Example of Printed Models

We have fabricated several objects for medical application by utilizing this method. Figure 4(d) shows the tubular shape (inner diameter is 4 mm, thickness of wall is 0.5mm). Those thin wall tubes are highly flexible, and they are expected to be utilized for artificial blood vessel or the surgical training model for the vessel suturing technique. In general, blood vessel is composed of the endocuticule (inner wall) and exodermis (outer wall). Control of the proportion of inks would enable such structure that weaves the soft portion and the relatively rigid portion.

Figure 6 shows the hollow vascular model of which inner diameter is within a range of 0.5 to 2 mm. This model are most likely be use for the surgical training model for the insertion of a micro-catheter, stent placement technique.

In addition, when the object data is reconstructed the medical data, such as DICOM (from CT / MRI), the patient's organ can be organized as a three dimensional model. This indicate that the surgeons are able to simulate to cut, suture, and other surgical operations with the real shape 3D model.

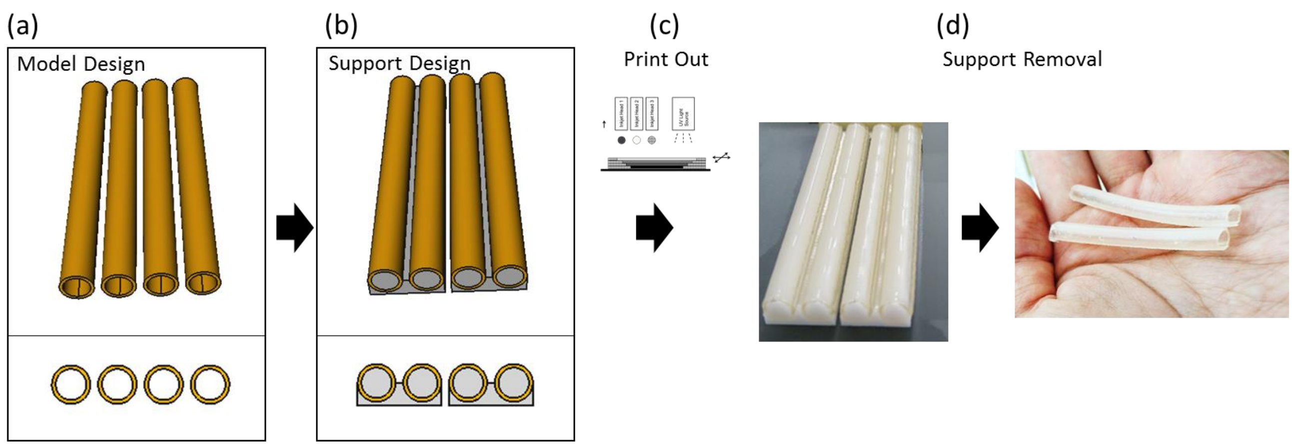
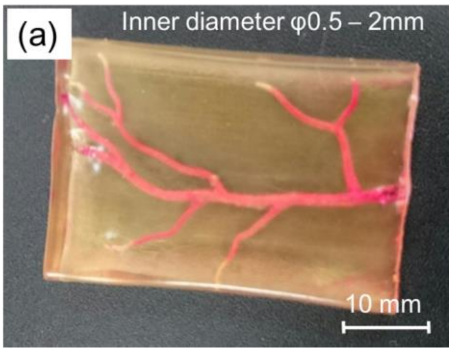


***Fig. 4** (a) 3D CAD designed model to fabricate. (b) Support structure. (c) Printed result. (d) Obtained samples by removing support.*



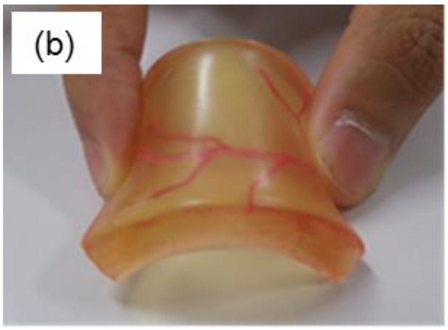


***Fig. 6** (a) The hollow vascular model. The bar represents 10mm length. (b) Bending the vascular model by hand.*

Conclusion

The direct inkjet deposition and UV irradiation system was developed to form the three dimensional hydrogel objects. We have succeeded in constructing the three dimensional NC gel objects. By controlling the proportion of the NC gel precursor ink and the diluent ink at the deposited surface, the compression modulus was varied from 0.02 MPa to 0.2 MPa.

Two types of medical applications, the tubular blood vessel, and the hollow vascular model were prepared. Those are expected to be used for the surgical training for medical doctors and students.

Most importantly, our goal is to enhance the quality of life of patients. Such surgical model has quite similar texture, and able to cut and suture. They might be able to give reality to surgical training and to give accuracy to surgical simulation.

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Author Biography

Yoshihiro Norikane obtained his master degree in chemical engineering at the University of Tokyo in Japan in 2003. He entered Ricoh. Co. Ltd. in 2003, and specialized in microfluidic, and inkjet head design, dynamic simulation of inkjet, and the ink formulation design. He is engaged in the development of Additive Manufacturing materials and systems.