

Fabrication of a Novel Bioceramic Membrane for Guided Bone Regeneration

Manami TODA, Kazunobu OSHIRO, Hirotaka FUJIMORI and Setsuo YAMAMOTO

Div. Applied Medical Engineering Science, Graduate School of Medicine, Yamaguchi University, 2-16-1, Tokiwadai, Ube-shi 755-8611

骨再生誘導を目指した新規生体セラミック膜の作製

戸田麻奈美・大城和宣・藤森宏高・山本節夫

山口大学大学院医学系研究科応用医工学系, 755-8611 山口県宇部市常盤台 2-16-1

In guided bone regeneration (GBR) technique, a barrier membrane is placed over the alveolar bone defect to prevent the down-growth of cells. However, the conventional membrane has no adhesive property for the tissue. This study challenged to develop a GBR membrane that has easily well adhesion to periodontal tissue with biocompatibility. [Received March 26, 2005; Accepted September 21, 2006]

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1. Introduction

Guided bone regeneration (GBR) is a current treatment for the defect of periodontal tissue. In GBR technique, a barrier membrane is placed over the alveolar bone defect to prevent the down-growth of cells.^{1,2)} However, the conventional membrane has no adhesive property for the tissue. Therefore use of screw to fix the membrane is necessary and difficulty exists in operation and complete sealing.³⁾⁻⁶⁾ As shown in Fig. 1, we focused on using hydroxyapatite (HA) and calcium alginate gel. Hydroxyapatite substrate was used as space maker and fast regeneration. Calcium alginate gel overcoat was for self-setting barrier. Resultantly, the membrane had semipermeable properties. In fabrication of HA substrate, the ink-jet printing was introduced to deposit hydroxyapatite inks with adequate control for material design. This study challenged to develop a GBR membrane that has easily well adhesion to periodontal tissue with biocompatibility.

2. Experimental procedures

Experimental procedure was shown in Fig. 2. First of all, Distilled water was used throughout for all reagents. 0.47 mol·dm⁻³ calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O; Lot PKJ3533, Wako, Japan) aq. was mixed with 0.33 mol·dm⁻³ diammonium hydrogen phosphate ((NH₄)₂HPO₄; Lot CEQ 2860, Wako, Japan) aq. under continuous stirring at 80°C controlled to the pH from 10 to 11 by the addition of ammonia solution to yield white precipitates. After 2h of boiling, the solution was cooled to room temperature and the precipitates were allowed to settle overnight. HA precursors were recovered from their mother liquors via vacuum filtration. The precipitates were treated hydrothermally at the temperature 200°C under the saturated vapor pressure for 10h to crystallize HA.⁷⁾

Then hydroxyapatite powders and additives were mixed to prepare the inks for applying to ink-jet printing system. The inks with the appropriate value of the ink characteristics, especially surface energy and viscosity can demonstrate the feasibility of using the system. Therefore, we determined these 2 factors. Second, the proper inks were using to control for a material design on an ink-jet transparency film (polyethylene terephthalate; PET). The organic matters like the PET film and several additives got rid of the drawing material by treat-

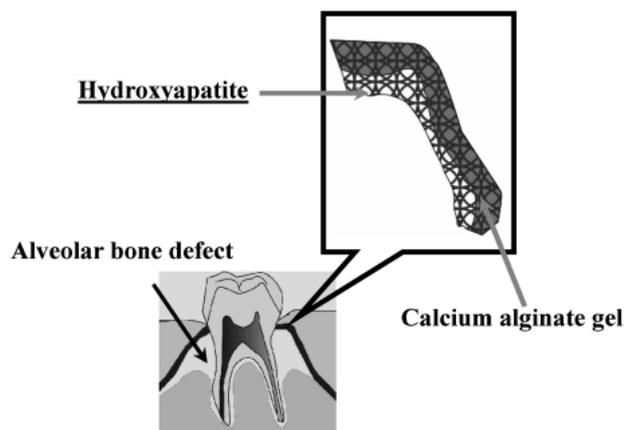


Fig. 1. Schematic illustration of a GBR membrane.

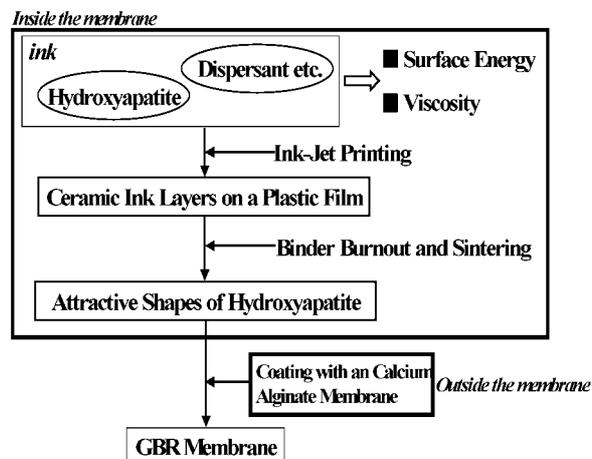


Fig. 2. Experimental procedure for fabrication of a GBR membrane.

ment with heating process. Furthermore the just inorganic material was tried to keep the shape with the pressing before

Table 1. Water-Based Inks Composition

Component	Function	Concentration %
Deionized water	Aqueous carrier medium	90
Hydroxyapatite	Primary ceramic	5
PEG 2000	Wetting, penetrating	4.5
KD6	Dispersant	0.5

the heating. Third, the calcium chloride solution was dropped onto HA material soaked in sodium alginate solution, a transparent elastic calcium alginate membrane was formed immediately. Composite material was accomplished by these processes.

3. Results and discussion

3.1 HA ink

Pretreatment was done in order to age the HA crystal sufficiently and obtain fine HA crystal particles. We believe that the Ca/P ratio of the HA powder sample suffered the pretreatment was close to the stoichiometric HA composition of 1.67. HA ink was prepared with the following chemical composition (Table 1). It is desirable that the solvent of inks is water-based from the aspect of biomaterial, harmony with the environment. For water-based inks of HA, HA particles tend easy to settle down because of its difference of specific gravity between the solvent and solute. And it is easy to agglomerate because HA particles are electrically charged condition.

KD6 is a detergent for dispersing HA particles evenly and preparing the stable suspension to prevent sedimentation and agglomeration. In general, in case of a lack of dispersant, the particle surface agglomerates because it cannot obtain the repulsion. However, if carried to excess, it induces the depletion. PEG is an excellent candidate because it is readily available in a wide range of molecular weights. Especially, molecular weight more than 1000 can avoid a peel of HA droplets on the substrate. It is easy to form the strong membrane. It is need to add PEG less than the solubility in order to obtain the smooth surface.

Droplets prepared HA ink were deposited on the glass slide and the water evaporated (Fig. 3). From the result, we found not only homogeneous droplet, but also agglomerate and cracking. Most effective factors of ink-jet printing inks are the characteristic of viscosity and surface energy of the liquid. The values of prepared inks were examined by following method.

The surface free energy of HA ink was calculated from the results of contact angle test by the Owen's method.⁸⁾ The Owen's method was usually widely used in the ology of surface free energy. This method is used these formulas as follows.

$$\gamma_L \cos(\theta + 1) = 2\sqrt{\gamma_S^d * \sqrt{\gamma_L^d}} + 2\sqrt{\gamma_S^p * \sqrt{\gamma_L^p}}$$

$$\gamma_L = \gamma_L^d + \gamma_L^p$$

In this study, distilled water and diiodomethane were used as two known liquids with two kind of substrates; Teflon and glass, and the values of γ_L^d and γ_L^p as shown in Table 2. After calculation, both γ_S^d and γ_S^p were obtained and then the surface free energy of HA ink was easily obtained (Table 3).

Furthermore, the coefficient of viscosity is obtained by the correlation between the driving electric current and the magnitude of viscosity used by the viscometer (Chichibu cement Co., VIBRO VISCOMETER; CJV-2000) as shown in Table 3.

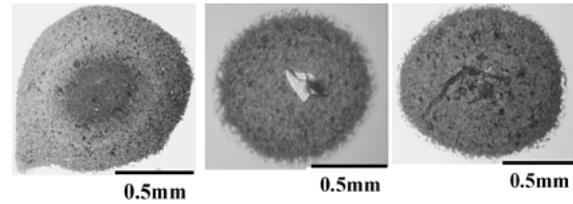


Fig. 3. HA ink droplets of micro-particle on the glass slide observed by optical microscope.

Table 2. The Dispersion (γ_S^d), Polar (γ_S^p) Components for Liquids. (Distilled Water and Diiodomethane are used as Dispersion and Polar Components, respectively)

Support	θ_{water}	$\theta_{\text{diiodomethane}}$	γ_S^d (mNmm ⁻¹)	γ_S^p (mNmm ⁻¹)
Teflon	124.4	69.6	23.1	0.855
Glass	31.7	41	39.1	28.6
γ_L^d (mNmm ⁻¹)	21.8	50.8		
γ_L^p (mNmm ⁻¹)	51	0		

Table 3. Comparison of the Characteristic between Hydroxyapatite Inks and other Ceramic Inks; Zirconia Inks and Aluminum Oxide Inks⁹⁾

Liquids	Surface energy γ_L / mNm ⁻¹	Viscosity / mPa·s, 25°C
Hydroxyapatite inks	61.3	8.6
Ceramic inks	25-70	1-10

After careful optimization, we could obtain the suitable characteristic of HA ink for ink-jet printing, considering other ceramic inks⁹⁾ a; zirconia inks and aluminum oxide inks as shown in Table 2.

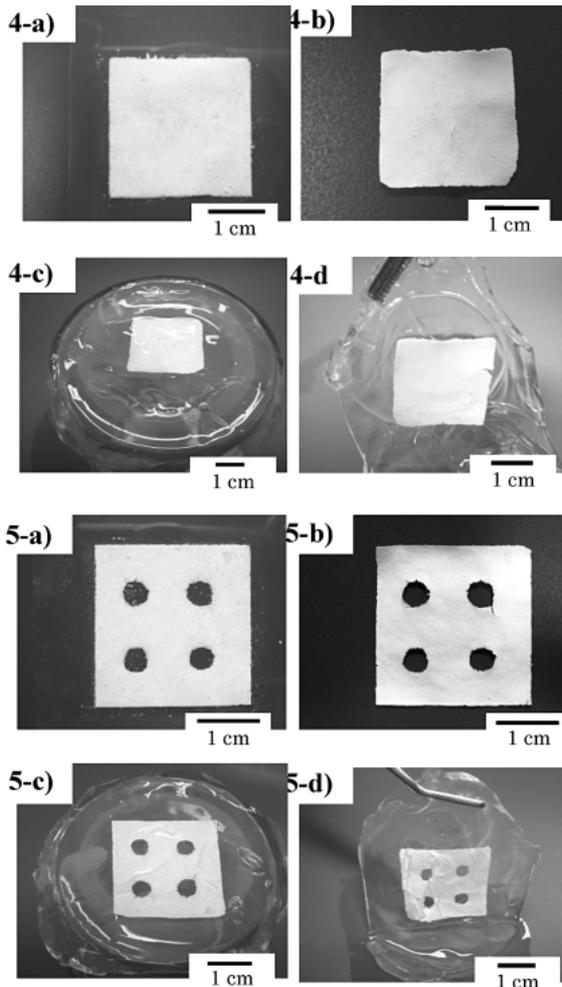
3.2 Printed material on an ink-jet transparency film

Pressed material on the ink-jet transparency film was realized with above-mentioned inks after printing using by PM-750C; EPSON, Japan (Figs. 4-a and 5-a). However, during printing, serious problems occurred such as nozzle clogging and inconsistency with image quality plagued the technology. Despite of these problems, the current solvent system was adopted because of fabrication of attractive design.

3.3 HA membrane

Printed material was pressed with pressing machine at 100 MPa to maintain the original shape. We carried out the schedule of heating rate; 1 degree C/min. using a heating oven, for both burnout of ink-jet transparency film as substrate for drawing and binder in the inks, and then, sintering. However, most of the sheets exhibited some degree of the cracking, bloating and destruction after sintering. These problems were attributed to the difference of the coefficient of thermal expansion between HA and the ink-jet transparency film.

The next heating schedule was extremely conservative after pressing at 200 MPa. The problems were solved by these efforts. The attempt indicated good sintering for maintaining the structure (Figs. 4-b and 5-b).



Figs. 4 and 5. Photographs of the specimens; a) pressed material after printing, b) HA membrane after both the burnout and sintering, c) and d) HA/calcium alginate membrane, respectively.

3.4 GBR membrane with calcium alginate gel

When calcium chloride solution was dropped onto HA material soaked in sodium alginate solution, a transparent elastic calcium alginate membrane was formed immediately (Figs. 4-c, d and 5-c, d). In actual dental treatment, calcium alginate membrane would be made on the surface of existing bone covered with HA membrane soaked in sodium alginate

solution and then dropping calcium chloride solution. GBR operation procedure will be simplified, because this material possesses adequate property that can be formed instantaneously on the surface.

4. Summary

Good potential of fabrication for novel GBR membrane has been proved in this study. Superior characteristics of the membrane will be expected in the following three points.

(1) The materials of membrane will have good biocompatibility and excellent tissue response.

(2) The membrane will be easily formed and have well adhesion to periodontal tissue.

(3) The membrane after surgery will be able to examine under the X-ray observation.

In this study, the composite material could be fabricated and it might be creatively used to control the duration of the GBR treatment.

Nomenclature

- γ_S : Surface free energy of the solid
- γ_S^d : Free energy of dispersion components
- γ_S^p : Free energy of polar components
- γ_L : Surface free energy of the liquid
- γ_L^d : Free energy of dispersion components
- γ_L^p : Free energy of polar components
- θ : Contact angle between the liquid and the solid

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