

The effect of cyanoacrylate infiltration on microstructure of hydroxyapatite/chitosan composite

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Abstract. Brittle nature of hydroxyapatite for bone implants reduced by adding chitosan. To strengthen the particles bond of the composite, cyanoacrylate was infiltrated into the composites. Infiltration was performed at room temperature and without any external pressure treatment system. The aim of this study is to examine the microstructure of hydroxyapatite-chitosan composite by infiltration of cyanoacrylate. Hydroxyapatite composite-chitosan composite was immersed in cyanoacrylate. Cyanoacrylate infiltrate into composite from all directions. The system is isolated from atmospheric air in order to avoid direct contact with air. Surface morphology was observed by scanning electron microscope on the specimen. Observations indicate that the higher content of chitosan, cyanoacrylate increasingly looks much infiltrated composite hydroxyapatite-chitosan.

INTRODUCTION

Hydroxyapatite (HA) bioceramics have porous morphology which results in good bonding capability to the bone, and a good mechanical interlock of the material. Dimensions and morphology of the pores can support bone osseointegration [1,2]. Although HA is superior in biocompatibility thereby making it a material of choice for bone implants [3], unfortunately, its mechanical properties is not as good as the mechanical properties of natural bone [4]. A wide range of materials for biomedical applications can be created based on two components, i.e., nanocrystalline apatite and chitosan [5,6,7,8]. Chitosan is a promising material for biomedical applications because it is biocompatible with human tissue, and its ability to facilitate the regenerative process in wound healing [9]. The HA has a low hardness and is brittle so it gives constraints in the design process [10] used the chitosan which was a natural biopolymer that is expected to be like the organic component of bone matrix and can cope with the fragile nature of HA, and the enhanced elastic modulus significantly was shown in macro-mechanical test.

Recently, biomedical material has been used cyanoacrylate with low viscosity as a tissue adhesive and bioimplant orthopedic [11,12]. Cyanoacrylate (CA) is suitable as a filler material of bone, increasing bone tissue bonding and new bone growth [13,14]. In this study, the cyanoacrylate was infiltrated into HA-chitosan composite without any pressure from outside the system. Infiltration effect of cyanoacrylate on the morphology of HA-chitosan composites were investigated using scanning electron microscope (SEM), furthermore the results of the investigation are discussed.

METHOD

Materials and manufacture

Materials used in this work are chitosan powder, bovine HA powder, and cyanoacrylate. Chitosan powder made from crab shells was mixed with bovine hydroxyapatite in a dry condition. The composite series of materials have different chitosan-HA weight concentration ratios, i.e. 0 wt.%, 10 wt.%, and 20 wt.% of chitosan. The HA was calcined on 500°C for 3 hr prior to mixed at 120 rpm and 30 min. Green bodies (12 mm diameter, 3 mm thick) of

HA-chitosan composites were successfully compacted and sintered using cold uniaxial compaction technique. In uniaxial pressing the specimens were compacted at 50 kg/cm², 75 kg/cm², and 100 kg/cm². Sintering was performed at 1000°C, and holding time for 1h.

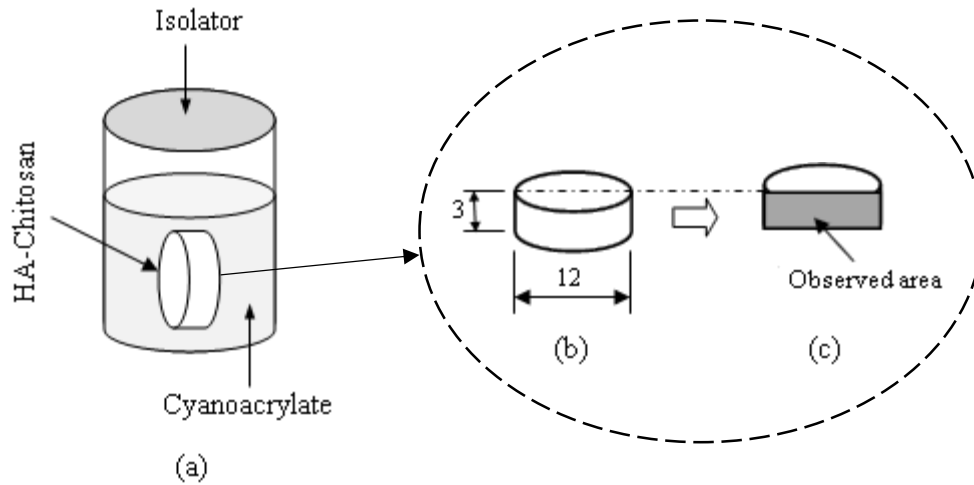


Fig. 2 Schematic diagram for (a) infiltration test, (b) sample HA-Chitosan, and (c) infiltrated surface of CA for HA-Chitosan composite

The CA-HA/Chitosan composites made by pressureless infiltration-assisted liquid technique. Liquid CA was infiltrated into a porous HA/Chitosan composites at room temperature in 24 hours. During the infiltration process, it was distributed in all directions, and was kept from direct contact with atmospheric air so that no polymerization of CA (see Fig. 1a).

Morphological test

The depth infiltration of CA on composite HA-chitosan (Fig. 1b) was observed using scanning electron microscope (SEM).

RESULT AND DISCUSSIONS

Surface morphology of calcined HA at compacting pressure of 50 kg / cm² with and without infiltration of cyanoacrylate is shown in Fig. 3.

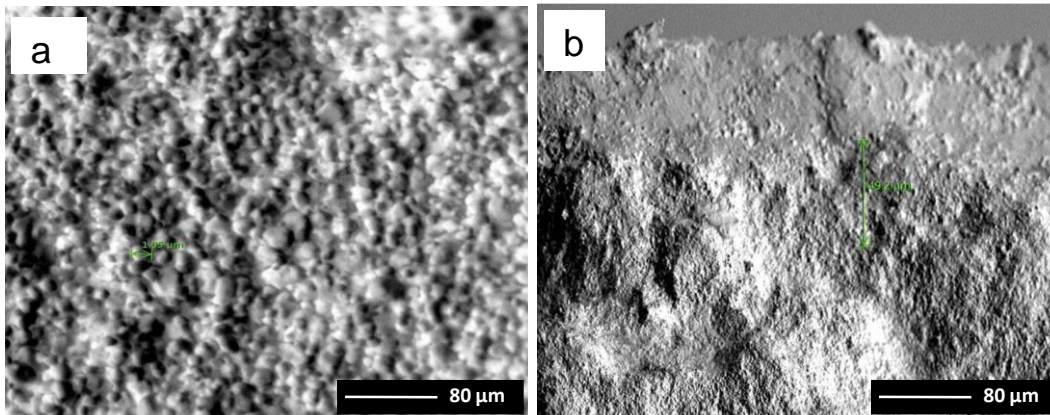


Fig. 3 Section Surface morphology of calcined HA calcined at compacting pressure of 50 kg/cm² without CA (a) and CA.

In case of composites without CA, the pores are clearly observed. Different conditions was seen in the infiltrated composite in which the pores are closed by cyanoacrylate that filled pores. From SEM observation, the composite HA-chitosan decomposes on the surface, bound by cyanoacrylate and then embed to the surface of composite. Cyanoacrylate fill the pores, especially near the surface of the composite to decompose (**Fig. 3**).

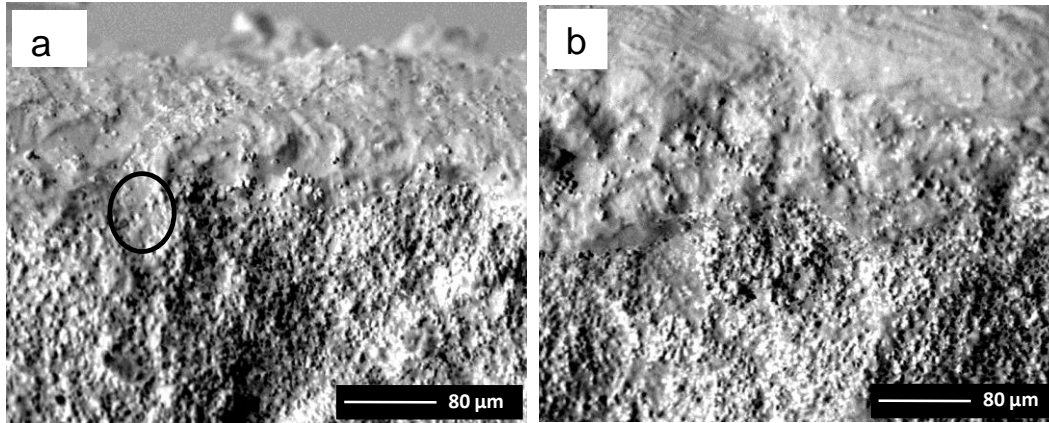


Fig. 4. Surface microstructure of HA-K composite on compacting pressure of 75 kg/cm². (a) and pressure of 100 kg/cm². Black circle indicated the infiltration of CA.

Fig. 4 depict a thin layer cyanoacrylate infiltrate the pores of the composite HA-chitosan which led to reduced composite porosity. Although infiltration occurred in the area in the middle of the composite section, however cyanoacrylate has not been able to fill the entire pores formed on the composite HA-chitosan. Cyanoacrylate infiltration occurred in many locations close to the surface of the composite, as shown in **Fig. 5**. In this area, the infiltration of cyanoacrylate capable of filling the pores of the composite HA-chitosan.

The entire surface was observed showed similarities phenomenon. The HA-chitosan composite is porous therefore CA is able to infiltrate that composite through the pores. Cross-section surface close to the surface in direct contact between the composites and cyanoacrylate has higher intensity on infiltration of CA. These conditions encourage cyanoacrylate able to fill the pores and into the bond between the particles previously separated by pore. Good adhesion of CA is able to increase the interfacial bonding between the particles hydroxyapatite. Increased interfacial bonding effect though small is to increase Young's modulus [15]. Good interfacial adhesion affect the behavior of the composite and the ability to transfer load will be increased by increasing the interfacial bonding strength [15].

CONCLUSIONS

Infiltration cyanoacrylate composite surface is a function of distance. The farther from the surface, cyanoacrylate infiltration decline that ultimately was not able to fill the pores of the composite. When the composite is in the cyanoacrylte, composite surface to decompose and the things that are the cause has not been evaluated.

REFERENCES

1. Le Huec, J.C, Schaefferbeke, T, Clement, D, Faber, J, Le Rebeller, A, *Biomaterials* 16. 113(1995).
2. Yoshikawa, H, Myoui, A. *J. Artif. Organs* 8. Pp. 131(2005).

3. Kim Y., Seo S., Moon H., Yoo M., Park I., Kim B., Cho C. Chitosan and its derivatives for tissue engineering applications. *Biotechnology Advances* 26, pp. 1-21(2008)
4. Guo, H.B, X. Miao, Y. Chen, P. Cheang, K.A. Khor. Characterization of hydroxyapatite-and bioglass-316L fibre composites prepared by spark plasma sintering, *Materials Letters*, 58, pp 304-307 (2004).
5. Yamaguchi, I., Tokuchi, K., Fukuzaki, H., Koyama, Y., Takakuda, K., Monma, H. and Tanaka, J. Preparation and microstructure analysis of chitosan/hydroxyapatite nanocomposites. *J. Biomed. Mater. Res.* **55** , 20–27 (2001)
6. Li, J., Chen, Y.P., Yin, Y., Yao, F. and Yao, K. Modulation of nano-hydroxyapatite size via formation on chitosan–gelatin network film *in situ*. *Biomaterials* **28** , 781–790 (2007).
7. Wang, L. and Li, C. Preparation and physicochemical properties of a novel hydroxyapatite/chitosan–silk fibroin composite. *Carbohydrate Polym.* **68** , 740–745 (2007).
8. Jiang, L., Li, Y., Wang, X., Zhang, L., Wen, J. and Gong, M. Preparation and properties of nano-hydroxyapatite/chitosan/carboxymethyl cellulose composite scaffold. *Carbohydrate Polym.* **74**, 680–684 (2008)
9. Muzzarelli, R.A.A. Chitins and chitosans for the repair of wounded skin, nerve, cartilage and bone. *Carbohydrate Polym.* **76**, 167–182 (2009).
10. Verma D, Katti KS, Katti DR, Mohanty B. Mechanical resposns and multilevel structure of biomimetic hydroxyapatite/polygalacturonich/chitosan nano composte. *Materials Science and Engineering. C*, **28**(3), 399–405 (2008)
11. Vanholder.R., Misotten.A., Roels. H., Matton.G. Cyanoacrylate tissue adhesive for closing skin wounds: a double blind randomized comparison with sutures. *Biomaterials* 14 (10), pp 737–742 (1993)
12. Bayer,I.S.,Tiwariand, M. K.C., Megaridis, M.K. Biocompatible poly(vinylidene fluoride)/cyanoacrylate composite coatings with tunable hydrophobicity and bonding strength. *Applied Physics Letters* 93, 173902 (2008)
13. Bhat .S., Askew M.J., Njus G., Smith D.J. Alkyl Cyanoacrylates as Space Filling Bone Adhesives. *J Appl Biomater.* Fall;3 (3):207-10. (1992).
14. Kyeong-Jun Park, Ji-Ho Park, Sang-Bae Lee, Doug-Youn Lee, Kyoung-Nam Kim, and Kwang-Mahn Kim. Bioactive Cyanoacrylate-based Filling Material for Bone Defects in Dental Applications. *Key Engineering Materials Vols.* 284-286. pp. 933-936 (2005)
15. Fu, S.Y., Feng, X.Q., Lauke, B., Mai, Y-W. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites. *Composites: Part B* 39: 933–961 (2008)