

Advances in Bioceramics and Porous Ceramics VII

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Advances in Bioceramics and Porous Ceramics VII

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*A Collection of Papers Presented at the
38th International Conference on
Advanced Ceramics and Composites
January 27–31, 2014
Daytona Beach, Florida*

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Preface

This issue contains the proceedings of the “Next Generation Bioceramics” and “Porous Ceramics: Novel Developments and Applications” symposia of the 38th International Conference and Exposition on Advanced Ceramics and Composites (ICACC’14), which was held from January 26-31, 2014 in Daytona Beach, Florida, USA.

A rapidly growing area of ceramic science & technology involves the development of novel ceramic materials that facilitate the diagnosis and/or treatment of medical conditions. Bioceramics researchers have recently developed several types of bioinspired and biomimetic ceramics, which imitate attributes of materials found in nature. The “Next Generation Bioceramics” symposium addressed several areas associated with processing, characterization, modeling, and applications of bioceramic materials. Topics covered by the symposium included processing of advanced bioceramic materials; bioinspired and biomimetic ceramic materials; biomineralization; self-assembly of bioceramic materials; inorganic-organic composite materials; nanostructured bioceramic materials; mechanical properties of bioceramic materials; *in vitro* and *in vivo* characterization of bioceramic materials; bioceramic materials for drug delivery; bioceramic materials for gene delivery; bioceramic materials for sensing; and bioceramic materials for dental applications. This symposium facilitated numerous productive discussions among various groups in the bioceramics community, including academic researchers, industrial researchers, governmental researchers, and graduate students.

There is an increasing need for components possessing designed porosity for various applications in several key areas such as environmental control, energy, defense and healthcare. In the “Porous Ceramics” symposium, the speakers discussed how they can tailor the characteristics of the porosity embedded in ceramic parts, including the total porosity, the average cell size, the cell size distribution, and the degree of interconnectivity among the cells. Papers on a wide range of topics were given, such as innovations in processing methods, including automated manufacturing, structure and properties, modeling and novel characterization tools, mechanical behavior, micro- and meso-porous ceramics, ceramic membranes, and applications of porous ceramics. The sessions were well attended and there was lively discussion

after each presentation, confirming the large interest that exists in the ceramics community, both in academia and in industry, for porous ceramics because of their unusual characteristics and widespread applicability.

We would like to thank the staff at The American Ceramic Society, including but not limited to Greg Geiger, Mark Mecklenborg, Marilyn Stoltz, and Marcia Stout, for making this proceedings volume possible. We would like to thank Anita Lekhwani and her colleagues at John Wiley & Sons for their support of this volume. We would also like to acknowledge the efforts of the authors and reviewers, without whom this volume would have not been possible. We also thank the leadership of the Engineering Ceramics Division of The American Ceramic Society, including Andrew Gyekenyesi, Sanjay Mathur, Tatsuki Ohji, Dileep Singh, Mrityunjay Singh, Sujanto Widjaja, and the 2014 Program Chair, Michael Halbig, for their tireless efforts. We hope that this volume becomes a useful resource for academic and industrial efforts involving porous ceramic materials and bioceramic materials. Finally, we hope that this volume facilitates advances in ceramic science & technology and contributes to the leadership of The American Ceramic Society in these emerging areas.

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Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of seven issues published from manuscripts submitted and approved for the proceedings of the 38th International Conference on Advanced Ceramics and Composites (ICACC), held January 26-31, 2014 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 38th ICACC hosted more than 1,000 attendees from 40 countries and approximately 800 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following 19 symposia and sessions.

Symposium 1	Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics
Symposium 5	Next Generation Bioceramics and Biocomposites
Symposium 6	Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage
Symposium 7	8th International Symposium on Nanostructured Materials and Nanocomposites
Symposium 8	8th International Symposium on Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT), In Honor of Prof. Stuart Hampshire

Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Virtual Materials (Computational) Design and Ceramic Genome
Symposium 11	Advanced Materials and Innovative Processing ideas for the Industrial Root Technology
Symposium 12	Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13	Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy
Focused Session 1	Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials
Focused Session 2	Advanced Ceramic Materials and Processing for Photonics and Energy
Focused Session 3	Rare Earth Oxides for Energy, Optics and Biomedical Applications
Focused Session 4	Ion-Transport Membranes
Special Session	2nd Pacific Rim Engineering Ceramics Summit
Special Session	3rd Global Young Investigators Forum

The proceedings papers from this conference are published in the below seven issues of the 2014 CESP; Volume 35, Issues 2-8, as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites IX, CESP Volume 35, Issue 2 (includes papers from Symposium 1)
- Advances in Solid Oxide Fuel Cells X, CESP Volume 35, Issue 3 (includes papers from Symposium 3)
- Advances in Ceramic Armor X, CESP Volume 35, Issue 4 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics VII, CESP Volume 35, Issue 5 (includes papers from Symposia 5 and 9)
- Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials, CESP Volume 35, Issue 6 (includes papers from Symposia 7 and 8)
- Ceramic Materials for Energy Applications IV, CESP Volume 35, Issue 7 (includes papers from Symposia 6 and 13)
- Developments in Strategic Materials and Computational Design V, CESP Volume 35, Issue 8 (includes papers from Symposia 2, 10, 11, and 12 and from Focused Sessions 1, 2, 3, and 4); the 3rd Global Pacific Rim Engineering Ceramics Summit; and the 3rd Annual Global Young Investigator Forum

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference atten-

dees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 39th International Conference on Advanced Ceramics and Composites (<http://www.ceramics.org/daytona2015>) January 25-30, 2015 in Daytona Beach, Florida.

To purchase additional CESP issues as well as other ceramic publications, visit the ACerS-Wiley Publications home page at www.wiley.com/go/ceramics.

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Volume Editors

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Bioceramics

INFLUENCE OF THE HYDROXYAPATITE POWDER PROPERTIES ON ITS PROPERTIES RHEOLOGY BEHAVIOR

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ABSTRACT:

One of the key issues involved in successfully achieving HA ceramic body without defects using colloidal processing technique, is the preparation of homogeneous and high solid loading HA ceramic suspension with suitable rheological properties. This could be achieved not only via adjusting the type and amount of the dispersing agent, but also via controlling the properties of the HA powder. The maximum solid loading suspension that could be prepared from the as received powder was found to be 14 vol%. This value is too low to be successfully applied in casting processes. While, the treatment of the as received powder via calcination process prior to suspension preparation was found to play a very versatile role. A solid loading of 57 and 59 vol% would prepare from HA powder calcined at 1000 and 1100°C, respectively with applying the optimum amount of sodium polyacrylate dispersant. The suspensions produced from the calcined powder was found to have acceptable rheological properties for casting processes in terms of low particle interaction, lower number of floc and floc network and higher fluidity.

INTRODUCTION

Nowadays, bone tissue engineering is regarded as the most promising approach in treating diseased or damaged bone tissue. The challenge in this approach is to develop suitable bone scaffold possesses suitable porosity as well as reasonable mechanical properties.¹ Among the various materials tested in this concern, hydroxyapatite (HA), which shows excellent biocompatibility with hard tissue and also with skin and muscle tissues with the fact that it do not exhibit any cytotoxic effects is recognized as the most appropriate material for bone tissue engineering.^{2,3} However, the main drawback in the application of HA ceramics is its poor mechanical properties and the difficulties in manufacturing parts of complex shapes.⁴ In recent years a large effort has been made to overcome these problems via the trials in developing different processing techniques for achieving more reliable bioceramic bodies. Colloidal processing technique could be the most promising way for achieving this objective.⁵ The colloidal processing offers the potential to fabricate bulk bioceramic body having a complex shape similar to the human bone through careful controlling the initial suspensions.⁶⁻⁸ This technique involves a colloidal dispersion of fine powder particles in a liquid medium and their consolidation into a homogeneous dense green body with minimum defects (both in number and size).^{9,10} Consequently, the particle dispersion is the limiting factor in this process which affecting both rheology and homogeneity of the final produced suspension. The HA suspension should have as high as possible solid loading and in the mean time not possesses too low viscosity to avoid critical segregation phenomena as well as not too high to avoid air entrapping and density gradient defects in the final sintered product. Accordingly, in order to produce well dispersed suspension the inter-particle forces should be highly controlled through modification of the reactivity at the solid liquid interface.¹¹⁻¹³ This could be achieved through promoting inter-particle repulsion by any or both of the following methods: 1- through controlling the particle surface charge either by adjusting the media pH or adsorption of dispersant on the particle

surface (electrostatic stabilization) and 2- through steric separation of individual particle by adsorption of neutral or charged large chain polymers onto the particle surface (steric or electrosteric stabilization).¹⁴⁻¹⁷ Acrylic based polymers which are dissociated to form negatively ionized polyelectrolyte, are commonly used as dispersant for HA suspension providing enhanced stability via electrosteric force.^{18,19} It worthy mentioned that all manuscripts dealt with colloidal processing of HA ceramic or studying the flow behavior of slurry prepared from it, a heat treatment step for the as received HA powder should be firstly performed. This heat treatment step modifies the physical properties of the powder in order to successfully produce high concentrated suspensions from it. This means that the type and amount of dispersant as well as the pH of the media in not the only controlling factors in developing homogeneous and highly concentrated HA suspension. The properties of HA powder in terms of surface area, pore volume, and particle size is a highly important factor. Accordingly, in order to prepare homogeneous and high solid loading HA suspension both dispersant (type and amount) and powder properties should be optimized. To the best of our knowledge, there is no manuscript thoroughly investigate in details the effect of changing the powder properties on the rheological properties of HA suspension. Herein a trial was made in order to understand how much the variation in the properties of HA powder affecting the flow behavior of the final produced suspensions. An extensive study on the rheological properties of suspensions produced from both as received powder and powder calcined at various temperatures were carried out.

3.1. EXPERIMENTAL

2.1. Materials

Hydroxyapatite powder used in this investigation was delivered from Riedel-de Haen Co. (Seelze, Germany). A stock of HA powder was firstly calcined at both 1000 and 1100°C. The various properties of both as received and calcined powders were shown in Table. 1.

Table 1. Properties of both as received and calcined HA powder

	As received powder	Powder calcined at 1000°C	Powder calcined at 1100°C
Mean particle size, μm	3.389	13.2	16.887
Surface area, m^2/g	73.867	5.157	1.895
Pore volume, cc/g	0.119	0.003	0.002
Zeta potential, meV	-13	-27	-36.7

The dispersant applied in this investigation is Acumer 9400 was supplied from The Dow Chemical Company, Midland, Michigan, USA. It is a water-soluble sodium salt polymer used to disperse and stabilize high-solids mineral slurries. It is anionic dispersant of sodium polyacrylate polymer (SPA) of solid content 41-43 wt% with a molecular weight of 3000-4000 g/mole.

2.2. Processing

Suspensions produced from both calcined and as received HA powders are prepared by adding the predetermined amount of powder gradually (for obtaining various solid loading suspensions). Both dispersant amount and suspension pH are kept constant at 3.6wt% and 11, respectively for all produced suspensions. To avoid it's contributing in affecting the rheological properties of the finally produced suspensions. The suspensions are then ball milled in a planetary mill for 24 hr using zirconia ball as milling media. The chosen of 24 hr milling time was based on the fact that 24 hour is the last time to promote deagglomeration by ball milling.²⁰

On the other hand to avoid grinding of powder during milling the volume of suspension was maintained at twice the total volume of the balls.²¹ After preparation of all suspensions at various solid loadings (as received and calcined) it is subject to rheology measurements.

2.2. Characterizations

The particle size distribution and mean particle size (d_{50}) were determined by the laser diffraction method (FRITSCH Model ANALYSETTE 22, Idar-Oberstein, Germany). One gram of the sample was suspended with 10 ml bi-distilled water, then the produced suspension (produced with hand shaking) was employed for measuring size analysis. The specific surface area (S_{BET}) as well as the pore volume of the powders was determined by BET method using a surface area analyzer (Autosorb-1, Quantachrome Instruments, USA).

A laser Zetameter 'Malvern Instruments Model Zetasizer 2000' was used for zeta potential measurements. A 0.1 g of sample was placed in 50 ml Bi-distilled water with pH modifiers; having the ionic strength of $2 \times 10^{-2} M$ NaCl. The suspension was conditioned for 30 h during which the pH was adjusted. After shaking, the equilibrium pH was recorded. Then 10 ml of the suspension was transferred into a standard cuvette for zeta potential measurement. Suspension temperature was maintained at 25°C. Zeta potential was measured as a function of pH (HNO_3 1M and NaOH 1M were used to adjust the pH). Five measurements were taken and the average was reported as the measured zeta potential. The isoelectric point (IEP) was identified at the pH axis crossing point. The rheological behavior of HA suspensions was determined using a Bohlin CVOR controlled stress rheometer (Bohlin Instruments Limited, Gloucester, England) with a truncated cone and plate geometry (a cone spindle with a smooth surface that has a diameter of 60 mm, a cone angle of 4° and a minimum gap width of 0.15 mm have been used for performing these measurements). The apparent viscosity and shear stress versus shear rate curves was measured for HA suspension of various volume fractions for as received, calcined and that containing various volume contents of starches. In stress viscometry mode, the shear stress data were acquired as a function of shear rate of an ascending series of discrete steps with a 1 min equilibration time at each step. Steady shear measurements were performed at a shear rate of $0.01 - 100 s^{-1}$ by incrementally changing the shear rate and measuring the shear stress after a determined equilibration time at each shear rate. The suspensions were presheared at appropriate shear rate for 30 s before the measurements to improve the reproducibility. The measurements were performed at constant temperature of 26°C, while during measurements the sample was covered with stainless steel cover to avoid liquid evaporation. On the other hand, the dynamic stress sweep experiments were performed in an oscillatory mode using the same equipment as well as the same geometry and same temperature.

3.2. RESULTS AND DISCUSSION

3.2.1. Rheological behavior of as received and calcined HA powder suspensions

In order to investigate how much the calcination temperatures affect the rheological properties of HA suspension, suspensions produced from calcined HA powder are prepared. The HA powder calcined at 1000 and 1100°C were used in preparing suspensions of 14 vol% solid loading. This is the highest solid loading produced from the as received HA powder (14 vol%). When solid loading was increased to be above 14 vol%, it was difficult to get dispersed suspension and actually the produced slurry had a paste like consistency. Figure 1, shows the viscosity-shear rate curves for 14 vol% solid loading suspensions produced from as received and calcined HA powder. All suspensions show a shear thinning behavior. Whereas, the viscosity largely decreases with increasing shear rate. The shear thinning behavior is usually associated with the slurry structure. At low shear rate, liquid is immobilized in empty spaces within floc and

floc network. As the shear rate increases, the floc and floc network break down, the entrapped liquid is released and a more order structure is formed in the flow direction.²²

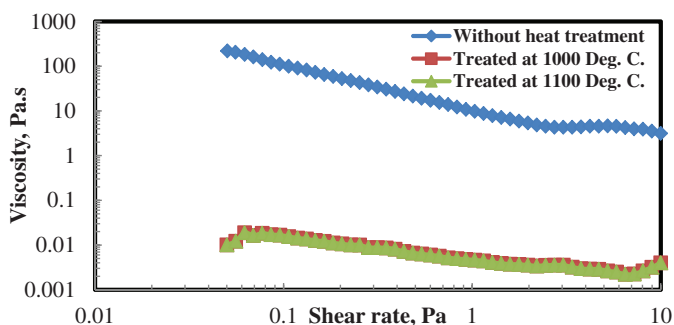


Fig. 1. Viscosity – Shear rate relationship of suspensions with solid loading of 14 vol%

It is obviously notice that the calcinations of the as received powder enhance to a large extent its flow behavior. A large deterioration in the viscosity was noticed when the powder is calcined at both 1000 and 1100°C, respectively, in the whole range of shear rate studied. This improvement in the rheological behavior is attributed to the large reduction of surface area of the HA powder upon calcinations.²³ The surface area of the as received powder was found to be about 74 m²/g, while, it is largely reduced to ~5, ~2 m²/g for powder calcined at 1000 and 1100°C, respectively (Table 1.). Not only that, but also it was found that the as received powder is characterized by high pore volume fraction compared to those calcined especially at 1000 and 1100°C (Table 1). The high increase in the viscosity of the as received sample is clearly a manifestation of its highly porous nature. Effectively, each individual HA particle acts as a “sponge” absorbing liquid, and, thereby, increasing the effective solids loading in suspension.²⁴⁻²⁶ The above mentioned results indicating that it is highly important to calcine the HA powder before suspension preparation. On the other hand it is possible to prepare homogeneous and high solid loading HA suspension only with the using of calcined HA powder.

3.2.2. Effect of solid loading on the rheology of suspension produced from calcined HA powder

The effect of different solid loading of powders calcined at both 1000 and 1100°C on the rheological properties of the produced suspension will be thoroughly investigated. The importance of this study is to determine the maximum solid loading of each powder that could be used in preparing the highly deflocculated suspension from HA. Different solid loading suspensions from both powders calcined at 1000 and 1000°C are prepared. The solid loading is varied from 14 to 59 vol%. Figures 2 and 3 show the viscosity – shear rate curves of HA suspension prepared from different solid loading of calcined HA powder at 1000 and 1100°C, respectively. The common features of both curves are that the suspension viscosity is increased with increasing solid loading as expected. In addition, all suspensions exhibit shear thinning behaviors, which could be attributed to the perturbation of the suspension structure by the shear. As suggested by Liu et al²⁶, at lower shear rates, the suspension structure is close to equilibrium state owing to the dominate effect of the thermal motion over the viscous force. While the shear rate increases, the viscous force affects the suspension structure and leads to a shear thinning behavior. At a very high shear rate, the viscous force even dominates and the viscosity plateau measured the resistance to flow of a suspension with a completely hydrodynamically controlled