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Review: nanocomposite of bioactive glass/ forsterite from raw material sand and egg shell for bone and dental implants

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Abstract. Bioactive glass has high bioactive, osteoconductive, biocompatible, and soluble properties in body fluids, but has low mechanical properties. This material has great potential for medical applications as a matrix in composites with forsterite fillers. The presence of non-toxic forsterite can improve the mechanical properties of bioactive glass. The development of the material (BG/F) using the sol-gel method can produce a nano-scale granule size (~ 19.6 nm) that corresponds to the size of the body cells. Apart from the size distribution and mechanical properties, the surface that is easy to bond with the bone is very interesting to study as an implant material. This narrative review analyzes the BG/F biocomposite associated with the use of sand and eggshells.

1. Introduction

The necessity of bone and dental implants in Indonesia is quite substantial. Indonesian Health Ministry (2018) recorded 5.113 fracture and 614.737 cavity and tooth loss cases that overcome bone replacing and implant installing [1]. Bone and teeth damage treatment has been done in various methods such as autograph and allograph. Autograph is a bone replacing by installing implants that come from the patient's body, meanwhile, allograph using donor implants. Both methods are less effective because of the risk of causing wound infection, potential morbidity of disease transmission, and limited numbers [2].

A biomaterial is one of an implant either from nature material or synthetic in a biological system to repair or replace tissue, organs, or function of body parts [3]. Types of biomaterials are biopolymer, bioceramics, biometal, and biocomposite. Each biomaterial has its own characteristic based on the function. Implants successes depend on its characteristic, there are non-toxic, bioactive, bioresorbable, biocompatible, and osteoconductive. Those meaning are 1) not poisonous and harmful to the body, 2) interaction occurs between implant and body, 3) implant can be absorbed by biological tissue, 4) capable to adapt to the body, and 5) stimulate osteoblasts in hard tissues [4].

Limitations in implant supply and high-priced reached about 400 USD per item generate biomaterial research development [5]. One of the potential biomaterials for this issue is bioactive glass/ forsterite (BG/F) biocomposite. BG (SiO_2-CaO-Na_2O-P_2O_5) matrix has been sold commercially and used as an implant extensively. The problems faced now are low mechanical properties [6] and synthesis still uses alkoxide precursors, such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS). Alkoxide precursors are harmful and expensive [7,8], poisonous [9] and difficult to be produced in big amounts. Raw material utilization aims to reduce harmful and expensive alkoxide precursor use [7]**.** Indonesia has plenty of raw material from sand and eggshell as biomaterial precursors. Sand is one of the SiO_2 sources with high purity, but its usage is very limited and exported as cheap raw material. Besides, the production of eggs in Indonesia keeps rising about 7.28% annually, Indonesian Directorate General of Animal Husbandry in 2009 recorded 0.90 million tons of eggs while in 2018 it's about 1.64 million tons [10]**.** Researchers believed using raw material in implant biomaterial manufacturing is more acceptable to the body because of the similarity of physical and chemical characteristics, bioactive, osteoconductive, and biocompatible [11]. Therefore, this paper review BG/F nanocomposite from sand and eggshell potency as biocomposite development innovation for bone and teeth implant.

2. Methods

Biocomposite BG/ F manufactured with commercial chemicals [12] meanwhile Indonesia has abundant raw material for biocomposite. Some researchers have successfully synthesized SiO_2 from various sand, including Tunisian sand for 99% [13], Nigeria sand for 98% [9], and Banjar sand for 97,16% [14]. Successful BG production with sand as starting material has been proven by the researcher [7, 9, 15, 16]**.** Besides, the Indonesian Agricultural Data Center and Information System (2015) recorded chicken egg production reach out to 1.64 million tons in 2018 [10]. About 12% of the egg is its shell, so about 196,800 tons of eggshells are obtained annually and calcined to gain ~61% of CaO [17] so Indonesia has about 120,048 tons of CaO every year as biomaterial raw material [18]. Eggshells contain high calcium from calcium carbonate ($CaCO_3$) (94%), calcium phosphate ($CaPO_4$) (1%), magnesium carbonate ($MgCO_3$) (1%) and other organic material (4%) [19]. Eggshell as a calcium source has been proven in some implant applications, for wollastonite synthesis [8], Hydroxyapatite (HA) [20], Hydroxyapatite Bio-Ceramic [19], biocomposite calcium phosphate/ chitosan [21], and calcium silicate ceramics [22].

2.1. Bioactive Glass Synthesis and Characterization

The bioactive glass was found in 1969 by Hench, shows its bioactive ability by forming a surface-to-surface bond by forming a HA layer on the surface when placed in tissue or immersion in simulated body fluid (SBF) [23]**.** HA's composition is quite similar to bone and able to form a strong bond between the implant and bone [24]. Bioactive characteristic in BG is an important component from injected material to replace and repair bone damage in orthopedic surgery or dental fillings [25]. Furthermore, BG can support cell gene regeneration [26], and genetic control of the osteoblast progenitor cell cycle, so cells can repair itself, fast proliferation, and osteoblast differentiation [23]**.**

Two common methods to form bioactive glass are melting and the sol-gel method [27]. The sol-gel method has its primacy than the melting method because the sol-gel method can decrease the degradation phenomenon during sintering, increase bioactivity, produce nanoscale material size, and efficient for tissue engineering application [28]. The sol-gel method was also suitable for BG synthesis using sand as raw material for SiO_2 source. BG raw material fourier transform infrared spectroscopy (FTIR) analysis result shows formation carbonate hydroxyapatite (CHA) during immersion in SBF [9], which is proven can increase bioactivity because of its similarity with apatite chemical composition in humans bone [29]. BG synthesis with sand as raw material is done by dissolving silica precursors in NaOH to produce metasilicate solution (Na_2SO_3). Then reacted with $Ca(NO_3)_2{\cdot}4H_2O$ solution, HNO_3

dan $NaH_2PO_4 \cdot 2H_2O$ solution. Heating BG gel in phase 70 ℃ for 72 hours, 130℃ for 42 hours), 700℃ for 2 hours, ends with 950℃ for 3 hours resulting density 0.494 g/cm^3 and high porous. SBF test shows reactivity, bioactivity, and degradability from HA formed in the BG surface. From Testometric OL11 INR, BG has 0.37 Mpa of compressive strength [16]. With same treatment, Adam (2015) got 1.17 Mpa of compressive strength. FTIR analysis shows the presence of combeite crystal ($Na_2Ca_2Si_3O_9$) and HA during SBF immersion [15].

2.2. Forsterite Synthesis and Characterization

Nano forsterite (Mg_2SiO_4, NF) has superior compressive strength and bioactivity in body fluid. Manual muscle test (MTT) shows the rate of osteoblasts spread keeps increasing consistent with planting time and absence of toxicity signs [30]. Forsterite degradation is lower than other silicate bioceramic making it suitable as a long-term implant filler and has an inhibitory effect on clinical isolate bacteria growth [31]. Forsterite can be produced from various starting materials such as SiO2 either commercial silica or natural sand with a high percentage of forsterite [32][33] [34]. Forsterite synthesis can be done in some methods, multi-step sintering (MSS) [35]**,** mechanical activity [36]**,** high energy milling [37] and sol-gel [32]**.** Various methods obtain forsterite with different amounts and sizes. Nurbaiti et al., (2018) using the mechanical activity method obtained 99.3% wt. of forsterite in nanoscale about 94 nm [38]**.** Sol-gel method obtaining nanoscale forsterite about 10-60 nm which is calcined in 700 ºC and 900 ºC [39]**.** Choudhary et al., (2018) calcined in 900 ºC and 1100 ºC produce a morphology like flakes showed from SEM analysis result [31]. Calcined forsterite at 950 ºC is the optimum temperature because it produces the highest compressive strength for 201 Mpa and modulus young for 4.8 GB. This shows that the heating process in forsterite greatly affects SiO_2-MgO composition [31].

Forsterite synthesis using sand as raw material by the sol-gel method has been done by mixing silica colloid precursor and $MgCl_2$ precursor. Establishing silica colloid by dissolving silica powder in 21 M of strong base and coprecipitation. The colloid product from coprecipitation is washed then added with distilled water to form a silica colloid precursor. $MgCl_2$ precursor is made by dissolving magnesium powder in strong acid. Forsterite sample from mixture of silica colloid precursor and $MgCl_2$ precursor is squeezed for 24 hours, then filtered and dried at 100 ºC. The sample is then heated at 900°C. X-ray diffraction (XRD) analysis result shows that forsterite formed in sample about 90.5 wt.% with an average crystal size about 53 nm [40]**.**

2.3. Biocomposite BG/ F Synthesis and Characterization

The advantage of biocomposite with the presence of forsterite is to increase BG matrix mechanical properties without lowering its intrinsic properties as bioactivity. BG/F biocomposite synthesis is done by mixing bioactive glass and forsterite with the amount of weight percentage that corresponds to the needs of implant application. The most commonly BG/F biocomposite mixing method is mechanical activity mixed with 0.1 wt.% cellulose carboxymethyl (CMC) as a binding material. Mixing using a ball mill for 30 minutes to ensure homogeneity and sintered at 1000°C for 2 hours [12,41]. The results of the universal testing machine (UTM) showed the addition of 30% NF to BG increased toughness by 0.22 Mpa.m$^{1/2}$ and lowered the Young modulus 5 times lower than the control sample.

Saqaei et al., (2015) calcined BG/F composites with NF variations of 10, 20, and 30 wt.% at 600 °C. MTT test results show biocomposite powder is non-cytotoxic. Nanocomposites containing 20 wt.% forsterite shows the best biocompatibility [42]. The addition of the right amount of magnesium in bioactive glass represents BG/F biocomposite potential for medical applications especially in bone defects treatment and dental implants [43]. Forsterite fillers have high mechanical properties and the highly bioactive BG matrix is a good BG/F biocomposite constituent as a biomaterial implant [41].

3. Result and Discussion

Structure characteristic of implant greatly affects the suitability of implant. The shape, inner structure, and implant design need to be adapted to the characteristics of the tissue to be replaced [44]. In addition, porosity, cavities, or microscale tract play an important role in cell proliferation and growth into implants [45]. In vivo studies show a decreased risk of infection as implant pore size increases after implantation. Nevertheless, the increase in pore size negatively impacts the mechanical properties of the implant [46]. The sol-gel method for developing (BG/F) biocomposite can be designed with surface properties, mechanical properties, and grain size distribution similar to natural bones. The sol-gel method can produce nanoscale biocomposite powder (~19.6 nm) [12].

The biological properties of (BG/F) biocomposite and its degradation in SBF are related to surface properties of implants which are the most important factors for achieving a high level of compatibility. Surface properties are a major factor in the success or rejection of implantable materials due to direct contact with the surface of host tissue [47]. In addition, surface roughness is the key to the level of osseointegration and implants mechanical fixation into the bone. Microscale surface roughness increases bone formation rate due to protein adsorption and cellular activity [47]. The results of (BG/F) biocomposite studies on a nanoscale and 10% NF percentage show optimal apatite development on sample surfaces analyzed with XRD, the apatite deposition phase on nanocomposite surface shows its bioactive properties [12]. In addition, Saqaei et al., (2015) show (BG/F) composite calcined at 600°C has a pure bioactive glass XRD pattern with amorphous phase characteristics without showing crystal peaks. The increase in forsterite nanopowder amount results in increased intensity and number of forsterite crystal peaks which means increased mechanical strength of biocomposite [42].

The biological and surface properties of biocomposites are strongly influenced by the calcination process and calcination temperature. (BG/F) biocomposite calcination at 600°C produces an amorphous phase, and calcination at 850-900°C produces a wollastonite-like crystal phase ($CaSiO_3$) which means biocomposite (BG/F) has advanced bio-functionality, excellent bioactivity, and biocompatibility [8]. The presence of Ca and Si ions in wollastonite demonstrates its important role in the formation of hydroxyapatite layers (HA), affects the mineralization process, and plays a role in bone bonding mechanisms [48]. Besides, the presence of wollastonite increases mechanical properties such as bend strength and higher crack toughness when compared to calcium phosphate and hydroxyapatite (HA) in bioactive glass 58S. Wollastonite crystal phase also leads to the release of ions from the crystal phase formed during the bioactive glass heating processes, such as Si^{2+} and Ca^{2+} into the SBF solution is more difficult than the amorphous composition because the glass-ceramic phase is thermodynamically more stable and the ions have a higher coordination number [42].

4. Conclusions

The use of sand as raw materials and eggshells is the latest innovation that has the potential to be a candidate for biomaterial raw materials. Its abundant availability in Indonesia enables the production of biomaterials on a large scale. Sand contains high silica and eggshells as a growing source of calcium each year. The use of sand is successful for the synthesis of bioactive glass and forsterite, and the use of eggshells is also very potential as a source of calcium in bioactive glass. The combination of BG/F materials used as biocomposite complements each other to increase their potential as bone and dental implants. Immersion in SBF indicates that forsterite has lower degradation than BG, making it suitable for implant life. BG matrix has good bioactivity and forsterite as fillers have high mechanical properties to complement the low mechanical properties of the BG matrix, so the mixture of both has the potential to produce (BG/F) biocomposite for medical purposes. This narrative review is expected to encourage the development of biocomposite research, particularly biocomposite repair (BG/F) developed from sand and eggshells so that the need for bone and dental implants is met.

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