Exp. Theo. NANOTECHNOLOGY 9 (2025) 147-156 https://doi.org/10.56053/9.S.147

Investigations on physico-morphology and spectral studies of fluorapatite-doped 46S19 bioactive glass hybrid biocomposites coated with gum Arabic and Ajwa seed powder for enhanced osteogenic applications

Hadeer Sh Ahmed[1,2,*], *Sadeer M. Majeed*[2], *Duha S Ahmed*[3], *Ali A. taha*[4]

[1]The National Nuclear, Radiological, Chemical and Biological Commission I-NRC, Council of Ministers, Baghdad, Iraq
[2]Medical and Industrial Materials Science Department, School of Applied Sciences, University of Technology, Baghdad, Iraq
[3]Applied Physics Department, School of Applied Sciences, University of Technology, Baghdad, Iraq
[4]Biotechnology Department, School of Applied Sciences, University of Technology, Baghdad, Iraq
[*]) Email: hadeershehab1993@gmail.com

Received 18/10/2024, *Received in revised form* 23/11/2024, *Accepted* 29/11/2024, *Published* 15/2/2025

In the biomedical field, there is increased interest in developing bioactive materials that have the ability to bond with hard and soft tissues of the human body. As the first biomaterials that will be used in the implants must themselves possess high osteogenic properties, many scientists have started manufacturing them. This work involved the preparation of the bioactive glass powder 46S19 and the fluorapatite powder FA using the sol-gel method with organic acid. The powders used in the preparation of hybrid biocomposites samples are identified using Fourier transform infrared (FTIR) spectroscopy to identify the presence of specific functional groups and phase composition, which are crucial for understanding the bioactivity. Pure bioactive glass and fluorapatite-doped bioactive glass of samples by increasing the concentrations of fluorapatite from 5 wt. % to 25 wt. % by pressing uniaxially at pressure of 624 MPs and sintered in air at 1000 °C temperatures for two hours have been synthesized. The resulting sintered samples are coated with a suspended solution of gum Arabic and Ajwa date seed powders to form hybrid biocomposites grafting material for bone implantation. Fabricated hybrid biocomposites samples are characterized through morphological analysis and physical tests. Emission scanning electron microscopy (FESEM) examination of proposed hybrid biocomposites samples showed the size of the particles as well as the bonding between them. The porosity and linear shrinkage of the study results showed that hybrid biocomposite samples slightly reduced with an increase the weight percentage of fluorapatite that acts as a filler in 46S19 BG.

Keywords: Bioactive glass; Fluorapatite; Sol-gel; Bioactivity.

1. INTRODUCTION

Advanced materials, including bioactive glasses, are gaining traction in tissue engineering, with research focusing on developing substances that promote bioactivation or are resorbed. Current orthopedic surgery materials, typically metallic, polymeric, or ceramic, are biocompatible and resistant to corrosion in the in vivo environment [1]. Since the discovery of the first bioactive material in the 1970s, bioactive glasses (BGs) caused a turning point in the field of biomaterials and have gained remarkable attention in various biomedical applications in the last five decades due to their special properties[2]. These materials replace many older types of materials, particularly those used to treat bone diseases [3], [4]. In general, bioactivity refers to the ability of the material to interact with the surrounding biological environment and have a beneficial effect on the host tissue by stimulating the attachment of biological tissues, the process of bone apposition, and the healing of the implicated tissue [5]. This study focuses on the routine use of bioceramics like bioactive glass (BG) and fluorapatite (FA), in response to the growing demand for bone graft substitutes. Bioactive glass is an artificial bioceramic that has been studied a lot and has been shown to work in clinical settings. It is biocompatible, osteoconductive, and osteoinductive, and it can bond to bone and skin, helping to restore bone or dentin [6]. Fluorapatite (FA) is another widely studied bioceramic with excellent biocompatibility and bioactivity because of its close similarity in composition to natural bone apatite [7]. It is now widely accepted that the presence of a FA phase in a bioactive system in general, and BGs in particular, enhances the mechanical strength of the material while reducing its brittleness, as demonstrated experimentally. Furthermore, the bioactivity performance of the already bioactive phases is significantly improved in bioglasses [8,9].

Recently, there has been a growing interest in plant-derived materials for the preparation of new hybrid biocomposites. Plants contain secondary metabolites (phytochemicals) with a wide range of bioactivity and low toxicity, and they have enormous potential for bone repair and regeneration [10]. Date palms (Phoenix dactylifera) typically discard Ajwa Date seeds as waste [11] . Ajwa date seeds are rich in cellulose fibers and bioactive compounds that are promising for biomedical and pharmaceutical applications [12]. Ajwa date seeds, when ground into powder, provide numerous benefits in research due to their high nutrient content, antioxidants, and anti-inflammatory effects [10]. They are rich in potassium, magnesium, copper, iron, calcium, phosphorus, niacin, and pyridoxine and can reduce oxidative stress and inflammation. Ajwa date seed powder is biocompatible, making it safe for use in biomedical implants and scaffolds [13]. Gum Arabic is a natural polysaccharide with various pharmaceutical actions, such as anti-inflammatory, biocompatibility, and sustained drug release. Gum Arabic is a natural adhesive that facilitates the binding of other materials, making it ideal for coating bioglass samples with date seed powder. It can also form a protective film on surfaces, controlling porosity and surface characteristics. Its water solubility makes it suitable for aqueous coatings [14], [15]. Coating with bioactive biomaterial is another way to improve the properties. A natural polysaccharide like gum Arabic improves the functional groups, which makes it easier for the date seed powder to stick to the substrate [16]. Therefore, the incorporation of Ajwa date seed powder into coatings could potentially enhance the surface characteristics and biocompatibility, aid in the biodegradation of bioglass-fluorapatite composites, contribute to mechanical stability, reduce surface porosity, aid in uniform distribution of date seed powder on the sample surface, and aid in the release of bioactive compounds for artificial bone graft material[17,18].

This study aimed to investigate the physical-chemical properties and morphology of hybrid biocomposites grafting samples, which are derived from pure bioactive glass 46S19 and fluoroapatite-doped bioactive glass 46S19 in different weight percentages (5%, 15%, and 25%) wt. The samples are

pressed uniaxially at a pressure of 624 MPs, sintered in air at 1000 °C temperatures for two hours, and then coated with a suspension of ajwa date seed powder and gum Arabic.

2. MATERIALS AND METHODS

2.1 Preparation of Bioglass Powder

The process involves hydrolyzing 22 mL of tetraethoxysilane in 200 mL of distilled water and ethanol, then adding 5 mM citric acid to achieve a pH of 2, dissolved 16 g of calcium nitrate hydrate, and added 11 g of sodium hydroxide to solution (A). A solution (B) is created by dissolved 2.5 g of ammonium dihydrogen phosphate in distilled water and NH_4OH, resulting in a pH of 10. The solution is stirred overnight, filtered, rinsed, and centrifuged. The cleansed gel is dried overnight. To test the impact of heat treatment on bioactive glass production, the dried powder is sintered at 700°C for two hours, resulting in a clear, stable, and homogenous product called powder [19], [20]. As shown in Figure (1).

2.2 Preparation of Fluorapatite Powder

To create fluorapatite sol, dissolve 12 g of hydrated calcium nitrate and 2.5 g of diammonium hydrogen phosphate in 40 mL of ethanol/water for two hours to achieve transparency. While stirring, add the aqueous solution to the alcoholic solution at a rate of 5 mL/min, and add NH_4OH to adjust the pH to 10. Gradually add and constantly mix a 0.58 g ammonium fluoride solution in ethanol/water with the previous solution. It stores the solution at room temperature for 20 days until it solidified into a homogeneous gel. The gels undergo centrifugation, rinsing, drying, and grinding, followed by sintering at 600 °C for 2 hours [21], [22]. As shown in Figure (1).

Figure 1 Preparation of Bioactive Glass and Fluorapatite Powders.

2.3 Fabrication of hybrid biocomposites samples

Four hybrid biocomposites Samples are produced, consisting of the pure bioactive glass sample and three samples of bioactive glass powder is mixed with fluorapatite different weight percentages (5%, 15%, and 25%) wt. The mixtures are prepared in a planetary ball mill for 1 hour to ensure a well-homogeneous powder. The resulting hybrid biocomposites powders are pressed damp in metal die, by pressing uniaxially at a pressure of 624 MPa to form cylindrical samples, sintered in air at 1000 °C temperatures for two hours.

To coat, date seed powder is made by extracting date seeds from fresh Ajwa dates in Jeddah, Saudi Arabia, soaking them in distilled water, removing adherent layers, washing, drying in an oven, crushing and grinding, and using a ball mill to create a fine powder. Gum arabic is prepared by dissolving 0.1 g in 50 mL of distillation water, mixing with 0.3 g of date seed powder, and agitating for 60 minutes in a stirrer magnetic. The mixture is then ultrasonically stirred in double-distilled water for 2 hours to create a homogeneous suspension. Samples are coated by immersing them in the suspension for 5 minutes, drying them in an oven at 60°C for 15 minutes, and repeating this process multiple times until completely coated. As shown in Figure (2).

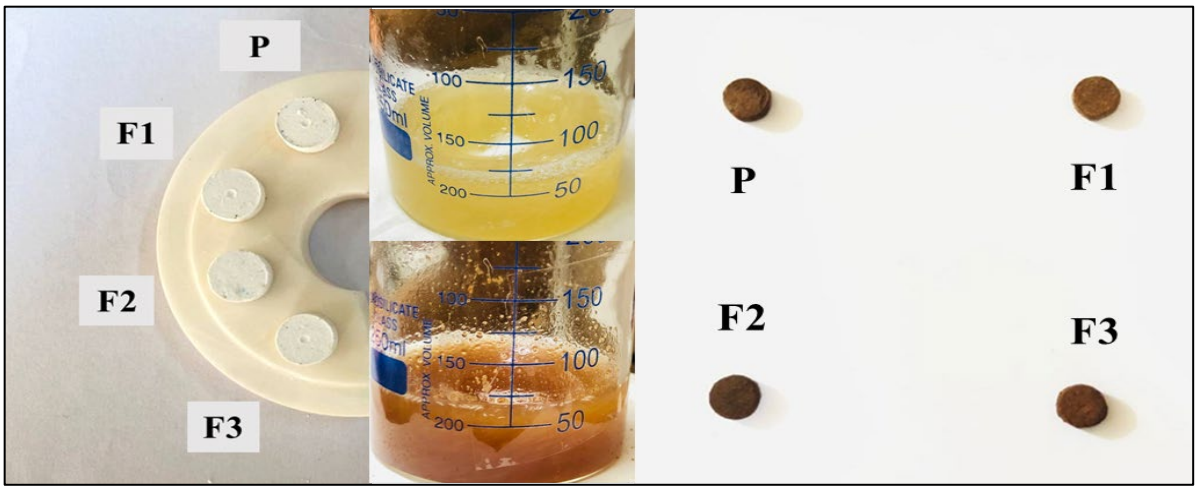

Figure 2 Preparation of hybrid biocomposites Samples.

Table 1 The chemical composition of hybrid biocomposites samples used.

No.	Sample Code	Basic Chemical Composition	Chemical Composition of Coating
1	P	BG	DS+GA suspension
2	F1	BG + 5 wt. % FA	DS+GA suspension
3	F2	BG + 15 wt. % FA	DS+GA suspension
4	F3	BG + 25 wt. % FA	DS+GA suspension

3. CHARACTERIZATIONS

3.1 Spectroscopy test

Fourier transform infrared spectroscopy (FTIR), spectra use a Bruker, Germany, scanner with such a scanning range from 400-4000 cm^{-1}, is performed to investigate the structural properties and functional groups of the powders prepared in hybrid biocomposites samples synthesis.

3.2 Microstructural analysis

Felid Emission Scanning Electron Microscope (FE-SEM) to study the microstructure of all prepared hybrid biocomposites samples. It coated samples with a thin layer of gold, which evaporated onto the sample surface, to prevent electrostatic charging of their surface.

3.3 Physical measurement

The porosity of hybrid biocomposites samples is measured using the Archimedes method, which involves boiling a dry sample in water for 35 minutes to remove trapped air, then cooling to ambient temperature, and weighing the sample for infiltration and immersion. The apparent porosity is calculated using the following equation [23].

$$(A.P)\% = (W_s - W_d)/(W_s - W_a) \times 100 \quad (1)$$

3.4. Linear Shrinkage Measurement

The length variation of hybrid biocomposites samples before and after sintering is evaluated using a Vernier caliper, and linear contraction is tested [23].

$$(L.Sh)\% = (L_o - L) / L_o \times 100 \quad (2)$$

4. RESULTS AND DISCUSSIONS

4.1 FTIR results

The FTIR spectrum is utilized to analyze the chemical bonds and microstructural properties of bioactive glass, fluorapatite, Ajwa date seed, and gum Arabic powders in the 500-4000 cm-1 wavenumber range, as depicted in Figures (4-3 a, b, c, d). The FTIR spectrum of BG powder, created using the sol-gel method, shows several bands, including characteristic peaks of Si-O stretching and Si-O-Si stretching at 941 cm^{-1} and 1087 cm^{-1}, bending vibrations at 474 cm^{-1} [24], [25], phosphate groups P-O stretching at 794 cm^{-1}, double peaks at 567 cm^{-1} and 651 cm^{-1}, 717 cm^{-1}, and weak peaks related to residual carbonate groups of precursors and hydroxyl groups at (3500–4000) cm^{-1}, as shown figure (3, a). [19], [26]. In figure (3, b) The FTIR spectrum of FA powder, obtained using the sol-gel method and heated to 600 ºC, shows apatite phosphate vibration bands at 466 cm^{-1}, 570 cm^{-1}, and 600 cm^{-1}. The bands at 964 cm^{-1}correspond to symmetric stretching vibrations of phosphate groups [27], [28], while bands at 1041 cm^{-1} and 1095 cm^{-1} correspond to asymmetric stretching vibrations. Absorption bands at 1431 cm^{-1} and 1454 cm^{-1}correspond to stretching vibrations of CO_2^{-3} group [29]. The FTIR spectrometer is used to analyze the functional groups of Ajwa date seed powder and gum Arabic powder [30], [31]. The spectra showed compounds like hydroxyl group signals, stretching vibrations of C-H bonds in aliphatic hydrocarbons, and C=O stretching vibrations of carbonyl groups in esters, ketones, and carboxylic acids. The spectra also showed C-H stretching vibrations at 1427 cm^{-1}, C=O stretching vibrations linked to carbonyl groups, and broad O-H stretching vibrations at 3390 cm^{-1} [32,33].

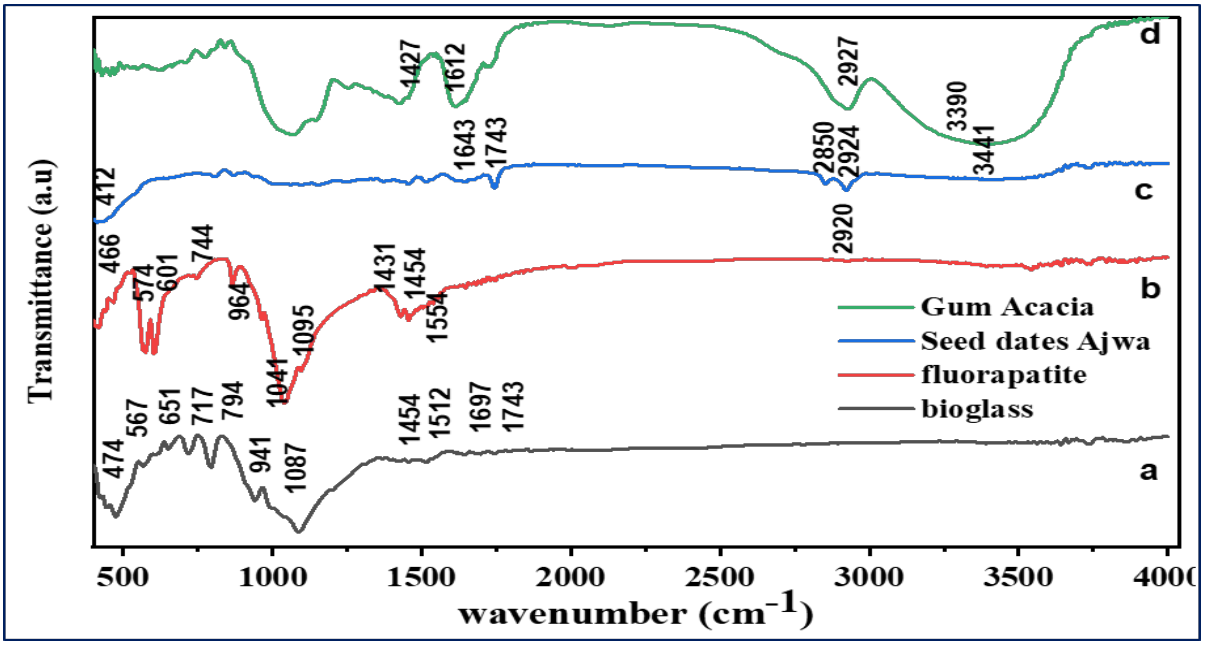

Figure 3 FTIR spectra of resulted samples a) Bioactive glass, b) Fluorapatite, c) Ajwa Dates Seed and d) Gum Arabic.

4.2 Results of FESEM

Figure (4 A, B) shows the FESEM images of sintered hybrid biocomposites samples at a temperature of 1000 ºC for 2 hour, coated with a suspension of (date seed powder + gum Arabic) with different magnification. The Pure hybrid biocomposite sample has particle sizes ranging from (145-558) nm with irregular shapes, that are related to clear association with the coating layer of agglomerated of particles [34]. In the hybrid biocomposites sample (5% wt.) of FA, the nanoparticles have a morphology range of (122-240) nm with irregular and spherical shapes, possibly related to the particles. In state nanoparticles of hybrid biocomposites samples (15% wt.) of FA and (25% wt.) of FA, the size of the nanoparticles is about (260–632) nm and about (66-386) nm, respectively, as shown in Figure (4 C, D). From the results above, it found the morphology showed that NPs are made up of irregular and spherical shapes that are uniform, possibly related to each other, and are in direct contact with the capping agent, the coating that generates indicating stabilization within the aggregation, in addition to being surrounded by pores. [35, 36].

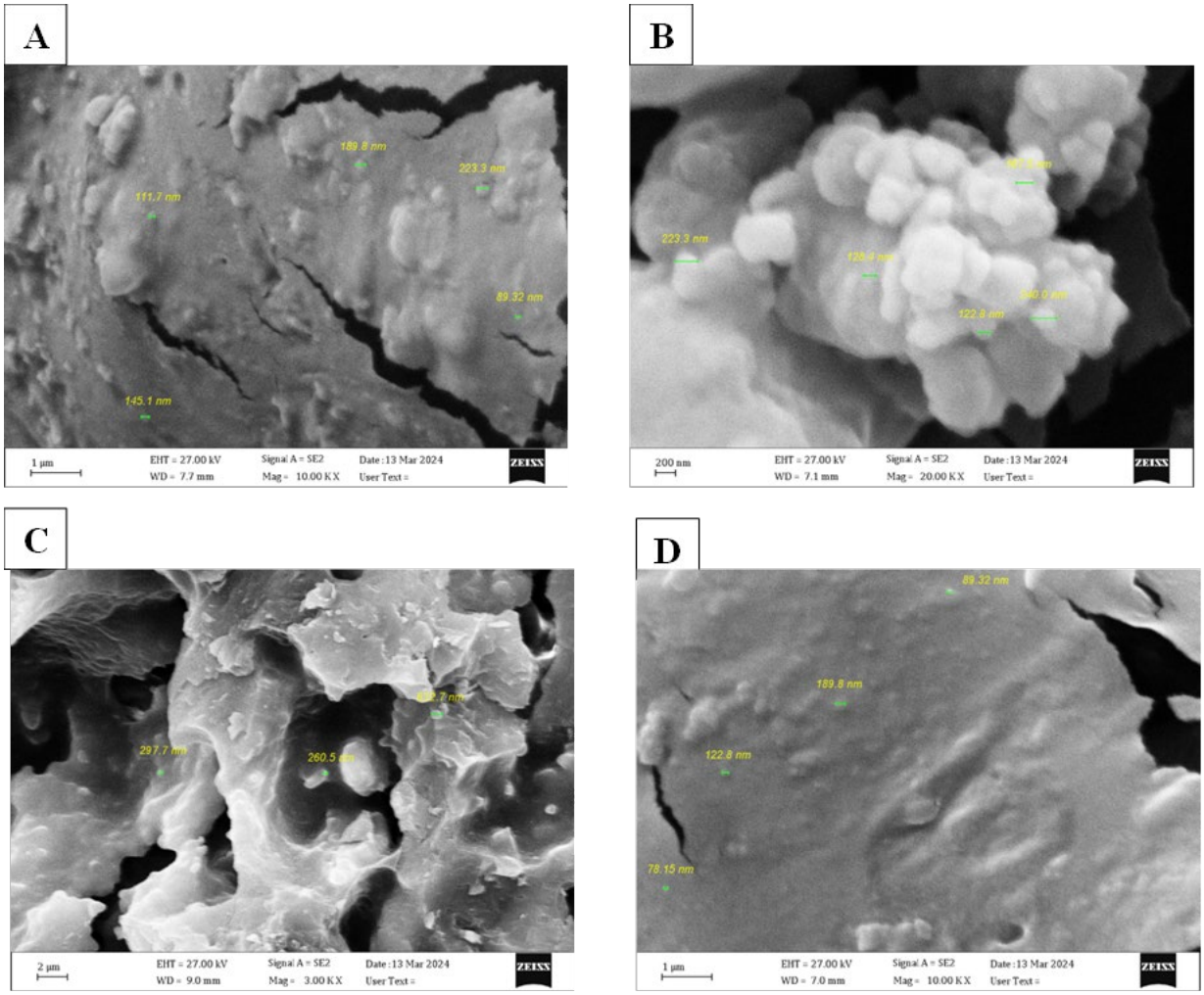

Figure 4 (A-D) FE-SEM images of hybrid biocomposites Grafting Samples with different magnification A) Pure (BG-DS) NPs at 1µm. B) (5% FA-BG-DS) NPs at 200 nm, C) (15%FA-BG-DS) NPs at 2µm, and D) (25%FA-BG-DS) NPs at 1µm.

4.3 Porosity measurement

The porosity of all hybrid biocomposites samples is measured using equation (1). When adding FA to bioactive glass, sintering at 1000 ºC, and coating with date seed powder and gum Arabic, a slight uniform decrease in pores is observed [37], [38]. The study shows that samples with a porosity similar to human bone are ideal for bone tissue engineering because they allow cells to grow and multiply efficiently and also make it easier for biomaterials to fit into natural bone [39,40].

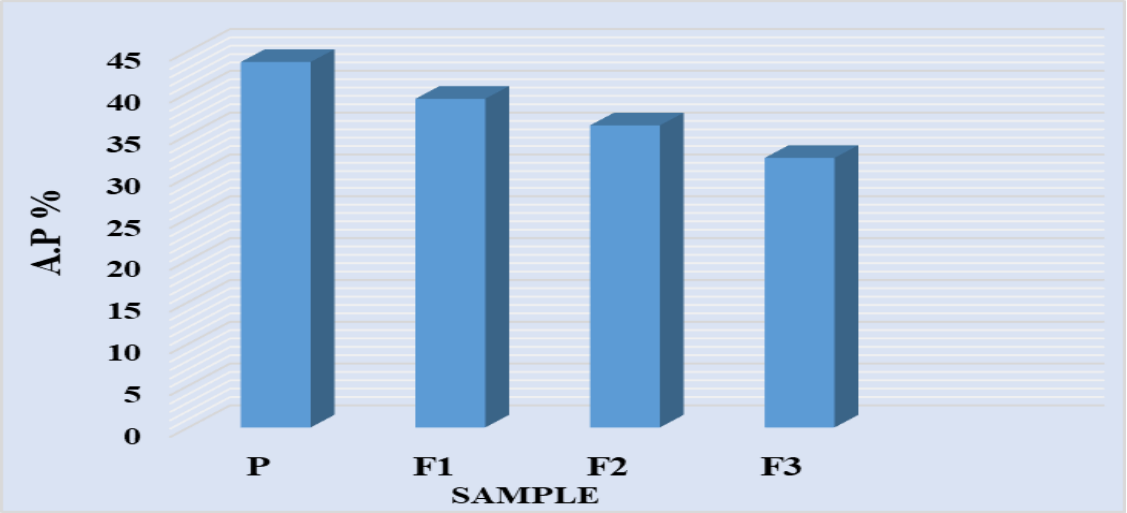

Figure 5 Porosity Measurement of All hybrid biocomposites Samples**.**

4.4 Linear shrinkage measurement

Sintering time, temperature, and diffusion species influence shrinkage, a material property where pores fill with solid material and cause the samples to shrink [41]. It calculates shrinkage percentages based on sample dimensions before and after sintering, comparing sintered samples with green samples. It uses a digital micrometer to estimate the mean linear shrinkage. Addition of FA to bioactive glass, sintering at 1000 ºC, and coating with date seed powder and gum Arabic results in a slight decrease in shrinkage [42-45].

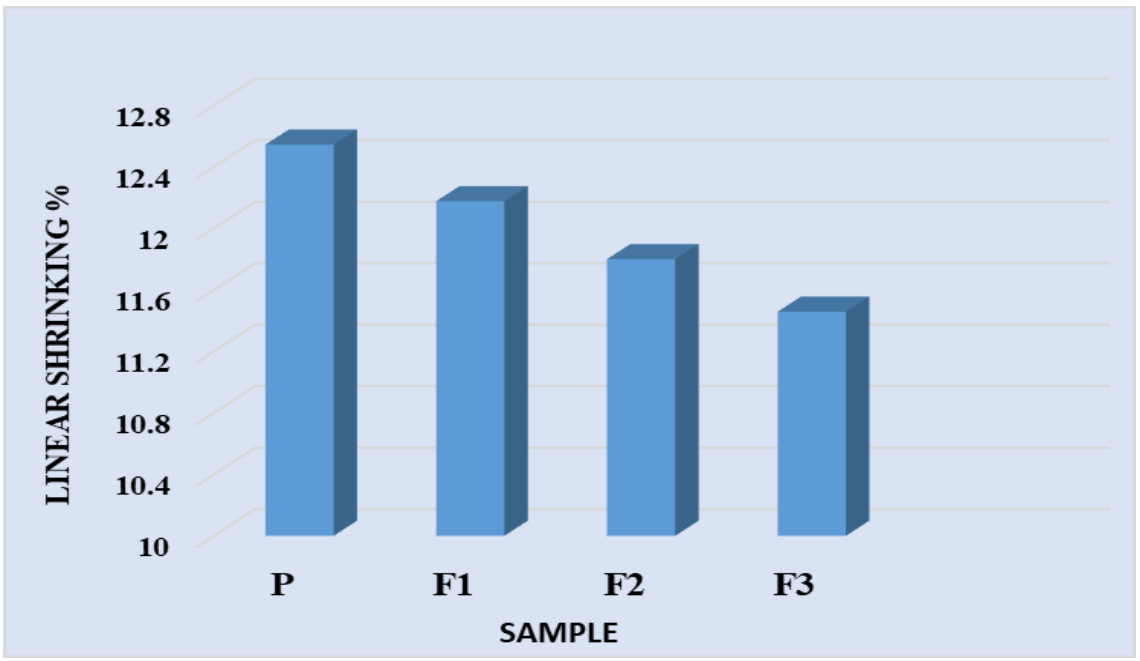

Figure 6 Linear Shrinkage of All hybrid biocomposites Samples.

5. CONCLUSIONS

A novel sol-gel method has been developed for producing bioactive glass and fluorapatite powders with varying compositions. The bioactive glass component was produced at 46% SiO_2, 30% CaO, 4% Na_2O, and 19% P_2O_5. Four hybrid biocomposites samples were created: the pure bioactive glass sample and three samples of fluoroapatite-doped bioactive glass with different weight percentages (5%, 15%, and 25%) wt. and sintered, coated with a suspension of ajwa date seed powder, and gum Arabic. FTIR spectroscopy has been shown to identify and detect the presence of specific functional groups and phase compositions of raw powders (bioactive glass, fluoroapatite, ajwa date seed, and gum arabic). FESEM analysis revealed varying sizes of particles and interconnected pores in hybrid biocomposites samples. The porosity and linear shrinkage of all hybrid biocomposites samples showed a slight decrease with increasing the weight percentage of FA to bioactive glass. Compared to the pure hybrid biocomposite sample, this results in the production of samples with an appropriate porous structure for bone implants.

References

[1] M. Arango-Ospina, A.R. Boccaccini, Tissue Eng. Ceram. Polym. 3rd Ed. (2022) 111
[2] L. Gritsch, Appl. Mater. Today 22 (2021) 100923
[3] S.M. Majeed, D.S. Ahmed, H.S. Ahmed, AIP Conf. Proc; 2019
[4] M. Hammed, M. Abbood, S. Majeed, Ann. Chim. Sci. Mater. 48 (2024) 137
[5] S. Majumdar, S. Gupta, S. Krishnamurthy, Biomater. Sci. 9 (2021) 8111
[6] A.A. Mehatlaf, A.A. Atiyah, S.B.H. Farid, AIP Conf. Proc. 2450 (2022)
[7] S. Manafi, F. Mirjalili, R. Reshadi, Enhanced Reader. 8 (2019) 77
[8] Z. Jawad, F. Mohammed, E. Al-hassani, Eng. Technol. J. 41 (2023)
[9] I.E.P. E. Souz, S.M. Carvalho, T. Martins, M.M. Pereira, Mater. Res. 23 (2020)
[10] S. Khalid, Trends Food Sci. Technol; 2017
[11] N.J. Abdulridha, A.M. Al-Ghaban, A.J. Al-Obaidi, Eng. Trans. 71 (2023) 185
[12] K. Narasimharao, J. Mater. Res. Technol. 18 (2022) 3581
[13] E. Moslemi, P. Dehghan, M. Khani, Contemp. Clin. Trials Commun. 28 (2022
[14] M. Farooq, Carbohydr. Polym. 156 (2017) 380
[15] V.U. Inegbedion, V.U. Okojie, F. Egharevba, Org. Polym. Mater. Res. 2 (2021) 13
[16] M. Keshavarz, P. Alizadeh, Int. J. Biol. Macromol. 167 (2021) 947
[17] S. Ghosh, N. Dandapat, V.K. Balla, Mater. Today Proc. (2015) 1326
[18] S. Mirza, ACS Omega 5 (2020) 11279
[19] J. Faure, Mater. Sci. Eng. C 47 (2015) 407
[20] T. Université, D.E. Rennes, Année; 2014
[21] H. Nasrellah, M. Rachid, M. Lamzouri, Mater. Tech. 110 (2022) 7
[22] V.D. Stanić, Z. Marić, B. Jović, Nucl. Technol. Radiat. Prot. 33 (2018) 180
[23] H.S. Ahmed, S.M. Majeed, D.S. Ahmed, J. Phys. Conf. Ser. 2114 (2021) 012064
[24] J. Faure, R. Jallot, C. Gauthier, Mater. Sci. Eng. C 47 (2015) 407
[25] P.K. Chakraborty, J. Adhikari, P. Saha, Mater. Adv. 2 (2021) 413
[26] H. Pirayesh, J.A. Nychka, J. Am. Ceram. Soc. 96 (2013) 1643
[27] S. Wei, X. Liu, C. Wang, Method Prod. Fluorapatite; 2010
[28] L. Borkowski, P. Nowak, K. Kowalski, Mater. Sci. Eng. C 116 (2020) 111211
[29] C.J. Tredwin, A.M. Young, E.A. Abou Neel, J. Mater. Sci. Mater. Med. 25 (2014) 47
[30] K.S. Allemailem, A.S. Alharbi, S.B. Faraj, Appl. Sci. 12 (2022) 94537
[31] S.A. Syed, M.S. Aldughaim, A. Bari, Food Anal. Methods 14 (2021) 5
[32] N. Thombare, A. Mahto, D. Singh, J. Polym. Environ. 31 (2023) 821
[33] M.A. Siddig, H. Adam, A.A. Siddig, Sudan Med. Monit. 8 (2013) 174
[34] S. Seyedmajidi, M. Hajisafari, F. Orand, Eurasian J. Anal. Chem. 13 (2018) 17

[35] G. Kirste, P. Weber, M. Schmidt, Sci. Rep. 14 (2024) 54228
[36] S. Manafi, F. Mirjalili, M. Hajisafari, J. Nanoanalysis 6 (2019) 145
[37] I. Cacciotti, M. Lombardi, A. Bianco, J. Mater. Sci. Mater. Med. 23 (2012) 4667
[38] N.J. Abdulridha, A.M. Al-Ghaban, A.J. Al-Obaidi, AIP Conf. Proc. (2024)
[39] E. Boccardi, A. Miriello, P. Torok, Ann. Biomed. Eng. 44 (2016) 1595
[40] M.S. Bahniuk, H. Pirayesh, J.A. Nychka, Biointerphases 7 (2012) 41
[41] R. Zhang, X. Li, Y. Wang, BMC Oral Health 21 (2021) 1931
[42] A. Motealleh, S. Eqtesadi, A. Civantos, J. Mater. Sci. 52 (2017) 775
[43] L. Lefebvre, L. Gremillard, J. Chevalier, Key Eng. Mater. 361 (2008) 265
[44] Oula Jabbar, Ali H. Reshak, Exp. Theo. NANOTECHNOLOGY 7 (2023) 41
[45] L. Li, S. Naher, Exp. Theo. NANOTECHNOLOGY 7 (2023) 55