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Effect of Incorporation of Lanthanum and Cerium-doped Hydroxyapatite on Acrylic Bone Cement Produced from Phosphogypsum Waste

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THIS study demonstrates the utilization of phosphogypsum waste for preparation of hydroxyapatite, lanthanum-doped hydroxyapatite and cerium-doped hydroxyapatite. Three concentrations of doping for each rare earth elements were prepared (0.25, 0.5, 0.75 weight %) respectively to be used as nanoparticles fillers additive to enhance the antibacterial activity, mechanical properties and bioactivity of conventional polymethyl methacrylate based bone cements. The prepared nanoparticles fillers are incorporated manually in 20 weight % to conventional polymethyl methacrylate bone cement to achieve polymethyl methacrylate cement composites. The results revealed that cerium-doped in 0.5 weight % with hydroxyapatite / polymethyl methacrylate cement composite permits remarkable increase in antibacterial activity against Staphylococcus aureus, while preserving a reasonably adequate compressive strength, and showed much higher calcium and phosphorus ions release (P-value $\leq$ 0.05). Within limitation of this study, the results are indicating the opportunity of the innovative bone cement for dental and orthopedic applications.

Keywords: Hydroxyapatite, Lanthanum, Cerium, PMMA, Phosphogypsum, Acrylic, Bone cement.

Introduction

Phosphogypsum (PG) is a wide spread industrial waste produced in large amount with the phosphoric acid manufacture using the wet process method[1]primary byproduct from phosphoric acid production, is accumulated in large stockpiles and occupies vast areas of land. Phosphogypsum is a technologically enhanced naturally occurring radioactive material (TE-NORM.PG recycling provides a chance to utilize this waste material as a source of production of nano-sized HAP material for dental and medical applications purpose and to get rid of this industrial waste at the same time.

The produced PG waste amount yearly in Egypt is very huge; their storage may cause serious environmental problems in addition to the financial loss. Consumption of this waste product by recycling into useful materials is important to solve the waste disposal problems. Moreover, the PG waste is considered as a non-harmful products as it is free from heavy metals which was investigated by Sahar et al, where PG was transformed into HAP and was utilized as filler in

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a composite material[2,3].

Hydroxyapatite (HAP); $Ca_{10}(PO_4)_6(OH)_2$, a synthetic analogous to the calcium phosphate found naturally in human bone and teeth. Nano-sized HAP is considered as promising biomaterial for dental and orthopedic applications. It is extremely biocompatible with bioactive properties and hence bonds to bone and promotes the formation of bone necessary for prosthetic osseointegration[4–6]. Bioactivity of materials could be investigated by measuring their calcium and phosphorus ion release[7].

Polymethyl methacrylate (PMMA) which is commonly referred to acrylic bone cement is considered as the gold standard for fixation of orthopedic implants into bone. This is because PMMA hardens within a reasonable time, is easily shapeable, and offers resistance to peeling, high surface hardness and high impact strength. Moreover, it permits structural support and mechanical stability along the prosthetic/ bone interface[8,9]as evidenced by data from long-term national joint registries. Despite these successes, mechanical failure of the cement mantle can result in premature failure of an implant which has lead to the development of a variety of techniques aimed at enhancing the mechanical properties of the cement, such as the addition of particulate or fiber reinforcements. This technique however has not transitioned into clinical practice, likely due to problems relating to interfacial particle/matrix adhesion and high cement stiffness. Mesoporous silica nanoparticles (MSNs. However all this merits of PMMA bone cement but it is still considered as bioinert, which may lead to fibrosis to the investing tissues, thus permits a poor bone bonding at the material-tissue interface leading to aseptic loosening of the cemented prosthetic implant[10]. Moreover, it is reported that the combination of PMMA/HAP composite provide satisfactory bioactivity and mechanical properties[11–13]strong requirements in biomaterials are still to be met, both in polymers andceramics substitute, repair and regeneration of hard tissues defects. In this framework, tremendous efforts in the biochemistry especially biomaterials field have greatly impacted the advancement of modern biomedicine. According to development of polymer and ceramics biomaterials utilized in orthopedics and dentistry; there are three different generations, namely first generation which include bioinert materials, second generation which include bioactive and biodegradable materials and recently the third generation (materials that designed to stimulate specific molecular responses. Previously, it was found that incorporation of 20 weight% HAP nanoparticles into PMMA composites give an acceptable compressive strength according to ISO 5833:2002 and ASTM F451-08[14].

The risk of bacterial adhesion into biomaterials during orthopedic surgery increases the failure of the whole operation. Thus incorporation of antibacterial agent into bone cement could be very beneficial. It was demonstrated that the Staphylococcus aureus bacteria is the most important bacterial species predominant in bone infection and show preferential ability for adhesion, growth and privileged upon the surface of metallic biomaterials[15].

Incorporation of some elements in minor traces to nano HAP particles induces antibacterial and antifungal activity to the composites than pure HAP only[16]. Recent studies were carried to doped some rare earth element in very small amount to HAP nanoparticles to improves their properties[17] as mechanical properties of HAP can be improved by the doping of lanthanum[18]. In addition, cerium-doped HAP could improve mechanical properties with a potent antimicrobial activity[19].

So, the present study aims to prepare lanthanum-doped HAP and cerium-doped HAP from phosphogypsum waste to be impregnated in 20 weight % to commercially available acrylic bone cement and asses the compressive strength, bioactivity by measuring calcium and phosphorus ion release and antibacterial activity of the prepared bone cement.

Materials and Methods

The PG waste was chemically analyzed to confirm absence of any heavy metals in our previous investigation[2].

Preparation and characterization of filler nanoparticles

The preparation and characterization of HAP nanoparticle fillers from PG waste was done as described previously[2]. PG and phosphoric acid (85%) were used as starting materials and

ammonia solution was used for pH adjustment. PG solution was mixed with the required amount of phosphoric acid with vigorous stirring and pH of the reaction was adjusted by ammonia solution to be 11. The reaction was completed after one hour. All the characterizations for HAP as XRD, EDX, FTIR TEM and SEM were done to evaluate its crystallinity, microstructure and particle size[2,20].

The prepared HAP nanoparticles were then doped individually by two rare earth elements lanthanum and cerium during the preparation using three different trial percentages of the doped rare earth elements (0.25, 0.5, 0.75 weight %) and the papered samples were dried and calcined at 900°C for 2 hours. For all prepared samples , the microstructure and particle size were investigated by SEM and TEM and also the Characteristic spectral groups were observed by using FTIR as described before[20].

The structure of both undoped and doped HAP was confirmed by X-ray diffraction (XRD) (Bruker-AXS D8 X-ray diffractometer, Germany). The obtained XRD patterns were compared with model patterns on the Joint Committee on Powder Diffraction Standard (JCPDS) databases.

Preparation of PMMA cement composites

The prepared HAP nanoparticles and PMMA (Cemex ® Isoplastic, Tecres, Italy) were manually mixed to give cement composite. The weight percentage of HAP nanoparticles was 20%. The control group was contained only PMMA with no fillers addition. The second group was contained both the PMMA and the prepared HAP nanoparticles filler. The third, fourth and fifth groups were a composites of PMMA and 20wt% lanthanum-doped HAP nanoparticles in percentages of (0.25, 0.5, 0.75 weight %) respectively. The sixth, seventh and eighth groups were a composite of PMMA and 20 wt% cerium-doped HAP nanoparticles in percentages of (0.25, 0.5, 0.75 weight %) respectively. The ingredients then were manually blended together till a proper mix was achieved. Once dough stage was reached, the cement composites were packed into their specific molds.

Assessments of PMMA cement composites

After setting of the mixed cements, all samples were removed from their mold and ground with silicon carbide papers (650-2000 grit), and then visually inspected for any defected samples.

Antibacterial activity test

Five disc samples for each group of 2 mm in height and 4 mm in diameter were prepared. The antibacterial activity of the samples was evaluated against Staphylococcus aureus. The antibacterial activity was evaluated using the standardized Kirby–Bauer disc diffusion method[21]. The Staphylococcus aureus ATCC 6538 bacterial strains were acquired. The samples were inoculated on Mueller-Hinton agar plates and then incubation at 37 °C for 24 hours, the inhibition areas were inspected. The total diameter of the inhibition zone in mm was for each measured. The survival rates of the Staphylococcus aureus bacterial strains were assessed.

Compressive strength test

Five cylindrical samples for each group (12 mm in height and 6 mm in diameter) were prepared according to standard specification for acrylic bone cement specified in the ASTM F-451-99 standard[22]. The compressive strength was measured using universal testing machine(Shimadzu Autograph AG-X plus 5 kN, Kyoto, Japan) at a cross head speed 20mm/min with load cell 5KN, the maximum failure load was monitored; accordingly the compressive strength was calculated.

Bioactivity test

The calcium and phosphorus ions release were used to assess the bioactivity of the prepared samples. Five disc samples for each group of 1 mm in height and 10 mm in diameter were prepared. The specimens removed from the mold and immersed in 50 cm^3 distilled water, then stored in an incubator (CBM 2431/V, Italy) at 37◦Cfor 21 days. After that, 12 ml of the immersion solution from each sample were withdrawn by a syringe after and filtered using 0.25 or 0.45 µm Millipore filters. The solutions were then assessed to determine the concentrations of calcium and phosphorus ions in mg/L using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Agilent 5100 Inductively Coupled Plasma-Optical Emission Spectrometer with

Synchronous Vertical Dual View, Tokyo, Japan).

Statistical analysis

One-way Analysis of Variance (ANOVA) and Tukey HSD test were used. The significance level was set at $P \leq 0.05$. All statistical analysis was done with IBM® SPSS® Statistics Version 20 for Windows (SPSS Inc., IBM Corporation; USA).

Results and Discussion

The realization of bone cement is influenced by their ability to chemically bond to the surrounding bone. The tissue response at the material-tissue interface to the biomaterials intervention affects the success rate of their applications. PMMA bone cement lack for the required bioactivity property and oseointegration to the bone[10,23]. HAP nanoparticles fillers permits high rate of bioresorbability and accelerated deposition of apatite minerals, which is a beneficial for bone natural repair and healing process with enhancement of compressive strength[24]. PG waste could be used as an appetite raw material source, which composed mainly of calcium with other impurities such as phosphates, sulfates, fluorides, Magnesium, iron and silica[2]. The weight percentage of HAP nanoparticles was adjusted in this work to 20 wt% which considered the most sufficient ratio that not cause deterioration in the mechanical properties and give a reasonable bioactivity[14].

The incorporation of small traces of the rare earth elements display high chemical activity and intensely alter the biomaterials performance[25]. Lanthanum could modulate bone cells activity. Furthermore, the addition of a very small concentration of lanthanum has negligible human toxic effects[26,27]. Cerium is a potent element trigger wound healing by cell proliferation, migration, tissue remodeling and enhances vascularization[28,29]5% and 10%, w/v %.A recent study of cerium nanoparticles suggested that the local tissue reactions was nominal and was it is well tolerated. Furthermore, no systemic toxicity or in vivo micronucleus induction was detected in the bone marrow by implantation test[30]. Quartz may be added to some dental materials to reduce the total amount of polymerization shrinkage of polymer by occupying volume and to induce radio-opacity of products which helps helpful in diagnostic purpose[31].

Staphylococci, in specific Staphylococcus aureus, are the predominant invasive bacterial strain associated with bone infections worldwide[32], thus it was selected as the strain of choice to be examined in the antibacterial investigation. According to the ISO 5833:2002 and ASTM F451-99 specifications[22], the bone cement should possess a minimum requirement of 70 MPa compressive strength for acceptable performance even in stress bearing area. Yet, it was noted that the higher percentage of HAP filler was associated with a reduction in the compressive strength of the composite[33].

The capability of a material to release calcium ions was responsible for stimulation of bone repair by deposition of mineralized tissue through the induction of BMP-2 expression and alkaline phosphatase activation[34].The calcium and phosphorus ions release after immersion of the specimens into solution done using ICP analysis. ICP analysis is the most common test used to determine the bioactivity of a material through quantifying the changes in ion concentration in the solution[7,35].The time interval of specimens immersion into solution were chosen according to previous studies which showed that after investigation of many time intervals that the calcium and phosphorus ion release concentration increase and remain constant between days 14 to day 21[36,37].

The previous chemical analysis of PG waste results was listed in (table 1) that confirm absence of any radioactive or heavy-metals element such as cadmium which could hinder the utilization of the waste into medical field[2].

TABLE 1: The chemical composition of PG.

SO^{2-}_4	41.5%	MgO	0.2%	H_2O	18.5%	Fe_2O_3	0.1%
CaO	29.25%	P_2O_5	0.8%	F^-	0.18%	SiO_2	9.5%

Furthermore, the microstructure of both dried HAP and calcined sample at 900 ^{0}C, in our previous study revealed that the morphology of HAP particles is spherical with an average diameter in the range of 54–74 nm[2].

The XRD pattern for both undoped and all doped samples of HAP filler calcined at 900^{o}Cis shown in Fig. 1. Regarding undoped HAP , the main crystalline phases were HAP [JCPDS(76-0694)] and β-TCP [JCPDS(70-2065)] and also another crystalline phase was occurred as pyrophosphate [JCPDS(71-2123)]. So, XRD results indicated that calcined HAP was partially decomposed into β-TCP and pyrophosphate as a result of calcination [38]. For all doped HAP with different wt % of La or Ce, the two main crystalline phases of HAP and β-TCP were also occurred with different ratios (table 2). There is no occurrence of impurities for rare earth oxides in all patterns which may due to the little amount of doping materials. For all calcined samples undoped HAP and doped HAP with La or Ce, the characteristic peak of quartz was occurred [JCPDS (71-2123)] due to presence of quartz in the starting material (PG) as described previously [2].

TABLE 2: Different ratios between HAP and β-TCP for doped samples.

doped samples wt %	% of HAP	% of β-TCp
0.25 % of La	51	36.5
0.5% of La	64	26
0.75 % of La	64.1	26.7
0.25 % of Ce	63	27
0.5 % of Ce	60	30
0.75% of Ce	55	36.5

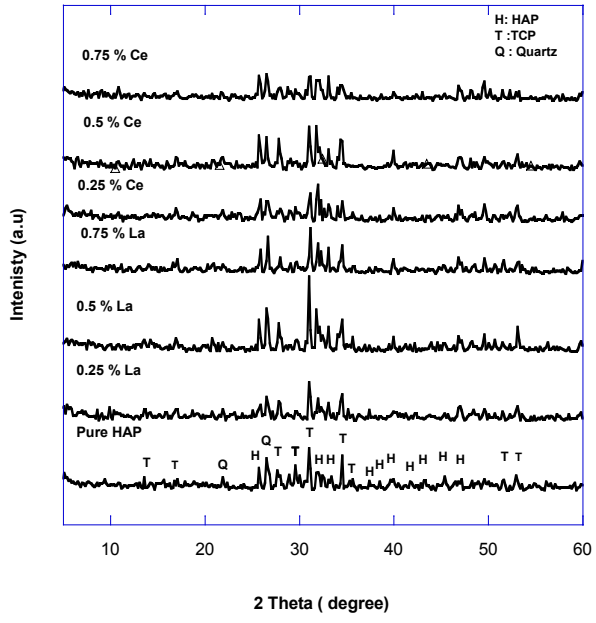

Fig. 1. XRD patterns of pure and doped HAP filler at 900^{o}C

Regarding antibacterial activity test, the bacterial inhibition zones values after 24 hour incubation period of specimens are listed in (Table 3). One-way ANOVA test results revealed a significant difference among all test groups (*P*-value ≤ 0.0001). Moreover, Pair-wise comparisons using Tukey's HSD test revealed that among all test groups; ***group 8*** had the highest significant mean values compared to ***groups 3-7***. This may be contributed to potent antibacterial activity of Ce than La which increased by increasing their doping concentration[19,39]. Meanwhile, among all groups, ***group 1 and 2*** had the lowest significant mean value and there was no significant difference between them. This may be due to lack of antibacterial activity of both PMMA and HAP.

TABLE 3: The mean, standard deviation values and results of one-way ANOVA and Tukey's HSD tests for comparison between bacterial inhibition zones of all groups.

Gp.1		Gp.2		Gp.3		Gp.4		Gp.5		Gp.6		Gp.7		Gp.8		P value
Control (PMMA only)		PMMA +HAP		PMMA+HAP+ Lanthanum1		PMMA+HAP+ Lanthanum2		PMMA+HAP+ Lanthanum3		PMMA+HAP+ Cerium1		PMMA+HAP+ Cerium2		PMMA+HAP+ Cerium3		
Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	0.0001*
0^{a}	0	0^{a}	0	3^{b}	0.1	4^{c}	0.1	5^{d}	0.1	7^{e}	0.1	8^{f}	0.1	9^{g}	0.1	

Means with different letters indicate statistically significance difference *; significant (p≤0.05).

Compressive strength mean values of the specimens are listed in (Table 4). One-way ANOVA test results revealed a significant difference among all test groups (P-value ≤ 0.0001). Moreover, Pair-wise comparisons using Tukey's HSD test revealed that among all test groups; ***group 1 and 2*** had the highest significant mean values compared to ***all other groups***. However ***group 2*** showed a lower significant mean values compared to ***group 1*** which may be attributed to presence of second phase HAP which may cause a weakening of the bond along the interface with PMMA matrix[13]. Meanwhile, among all groups, ***group 5 and 8*** had the lowest significant mean value. The decreased value of compressive strength may be due to occurred third phases such as β-TCP[18]. Moreover, ***group 4 and 7*** had a lower significant mean value compared to group ***3 and 6***, but they exceeded the minimum compressive strength of requirements of 70 MPa for acrylic bone cement according to ASTM F451-08[22].It could be noted that when HAP particles are mixed as an additive without coupling they may be agglomerated and act as crack initiation sites that impaired the mechanical strength[13].

TABLE 4: The mean, standard deviation values and results of one-way ANOVA and Tukey's HSD tests for comparison between compressive strength test of all groups.

Gp.1		Gp.2		Gp.3		Gp.4		Gp.5		Gp.6		Gp.7		Gp.8		P value
Control (PMMA only)		PMMA +HAP		PMMA+HAP+ Lanthanum1		PMMA+HAP+ Lanthanum2		PMMA+HAP+ Lanthanum3		PMMA+HAP+ Cerium1		PMMA+HAP+ Cerium2		PMMA+HAP+ Cerium3		
Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	0.0001*
126.8^{c}	0.7	94.8^{d}	0.7	86.2^{c}	1.3	77^{b}	0.6	58^{a}	1.4	85^{c}	1.4	76^{b}	0.9	59^{a}	0.6	

Means with different letters indicate statistically significance difference *; significant (p≤0.05).

Regarding bioactivity test, calcium and phosphorus ions release concentration values after 21 days of specimens' immersion in distilled water are listed in (Table 5 and 6). One-way ANOVA test results revealed a significant difference among all test groups (P-value ≤ 0.0001). Moreover, Pair-wise comparisons using Tukey's post-hoc tests comparisons revealed that among all test groups; for calcium and phosphorus ion concentration, ***group 8*** had the highest significant mean

calcium and phosphorus ion concentration values compared to other groups. The high dissolution tendency of cerium doped HAP than lanthanum doped HAP specimens may be due to the presence of β-TCP which is less stable than HAP and hence more soluble in aqueous environments[40]

Meanwhile, among all groups, ***group 1*** had the lowest significant mean calcium and phosphorus ion concentration value. This may be due to lack of bioactive HAP which acts as a source of calcium and phosphorus ions than in the other groups.

TABLE 5: The mean, standard deviation values and results of one-way ANOVA and Tukey's HSD tests for comparison between calcium ions release of all groups.

Gp.1		Gp.2		Gp.3		Gp.4		Gp.5		Gp.6		Gp.7		Gp.8		P value
Control (PMMA only)		PMMA +HAP		PMMA+HAP+ Lanthanum1		PMMA+HAP+ Lanthanum2		PMMA+HAP+ Lanthanum3		PMMA+HAP+ Cerium1		PMMA+HAP+ Cerium2		PMMA+HAP+ Cerium3		
Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	0.0001*
0.3^{a}	0.1	6.3^{b}	4.3	10.1^{c}	0.1	12.3^{c}	0.1	$18^{d,e}$	0.1	10.9^{e}	0.1	17.2^{d}	0.1	21^{e}	0.3	

Means with different letters indicate statistically significance difference *; significant ($p \leq 0.05$).

TABLE 6: The mean, standard deviation values and results of one-way ANOVA and Tukey's HSD tests for comparison between phosphorus ions release of all groups.

Gp.1		Gp.2		Gp.3		Gp.4		Gp.5		Gp.6		Gp.7		Gp.8		P value
Control (PMMA only)		PMMA +HAP		PMMA+HAP+ Lanthanum1		PMMA+HAP+ Lanthanum2		PMMA+HAP+ Lanthanum3		PMMA+HAP+ Cerium1		PMMA+HAP+ Cerium2		PMMA+HAP+ Cerium3		
Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	0.0001*
0.1^{a}	0	7.3^{c}	0.1	6.4^{c}	0.1	8^{f}	0.1	5.8^{b}	0.1	6.8^{d}	0.1	8^{f}	0.1	9.6^{g}	0.1	

Means with different letters indicate statistically significance difference *; significant ($p \leq 0.05$).

The results of this research demonstrated that cerium-doped in **0.5 weight % with HAP** has a high significant difference among all groups when considering antibacterial activity, compressive strength and calcium and phosphorus ions release value.

Conclusions

This study revealed that HAP nanoparticles which prepared easily from phosphogypsum waste can be used as fillers for dental and orthopedic applications. Moreover, cerium is a promising element when doped in 0.5 weight % with HAP to form nanoparticles filler when mixed in 20 wt% with the commercial acrylic bone cement permits an excellent antibacterial activity against Staphylococcus aureus, with sufficient compressive strength that exceed the minimum requirements of the acrylic bone cement, with enhanced bioactive property regarding calcium and phosphorus ions release. In conclusion, the presented in vitro results encourage further in vivo study regarding cerium-doped hydroxyapatite.

Conflicts of Interest

The author declares no conflict of interest.

References

1. El-Didamony H, Gado HS, Awwad NS, Fawzy MM, Attallah MF. Treatment of phosphogypsum waste produced from phosphate ore processing. J Hazard Mater 2013;244–245:596–602. doi:10.1016/j.jhazmat.2012.10.053.

2. Mousa S, Hanna A. Synthesis of nano-crystalline hydroxyapatite and ammonium

sulfate from phosphogypsum waste. Mater Res Bull 2013;48:823–8. doi:10.1016/j.materresbull.2012.11.067.

3. Hanna AA, Abu-Ayana YM, Ahmed SM. Phosphogypsum utilization - Part III: as adhesive filler and composite materials. J Mater Sci Technol 2000.

4. Abd El Hallem SM, Ghayad IM, Nassif N, Shoeib MA, Maamoun MA, Soliman H. Surface modification of Mg-3Zn-0.8Ca alloy using dual micro-arc oxidation (MAO) and fluoridated hydroxyapatite (FHA) coatings. Egypt J Chem 2014;57:97–108.

5. Aghyarian S, Hu X, Haddas R, Lieberman IH, Kosmopoulos V, Kim HKW, et al. Biomechanical behavior of novel composite PMMA-CaP bone cements in an anatomically accurate cadaveric vertebroplasty model. J Orthop Res 2017;35:2067–74. doi:10.1002/jor.23491.

6. Dorozhkin S V. Calcium Orthophosphates as Bioceramics: State of the Art. J Funct Biomater 2010;1:22–107. doi:10.3390/jfb1010022.

7. Hamdy TM. Bioactivity: A New Buzz in Dental Materials. EC Dent Sci 2018;17:1278–83.

8. Slane J, Vivanco J, Meyer J, Ploeg HL, Squire M. Modification of acrylic bone cement with mesoporous silica nanoparticles: Effects on mechanical, fatigue and absorption properties. J Mech Behav Biomed Mater 2014;29:451–61. doi:10.1016/j.jmbbm.2013.10.008.

9. Robo C, Öhman-Mägi C, Persson C. Compressive fatigue properties of commercially available standard and low-modulus acrylic bone cements intended for vertebroplasty. J Mech Behav Biomed Mater 2018;82:70–6. doi:10.1016/j.jmbbm.2018.03.001.

10. Lopes PP, Garcia MP, Fernandes MH, Fernandes MHV. Acrylic formulations containing bioactive and biodegradable fillers to be used as bone cements: Properties and biocompatibility assessment. Mater Sci Eng C 2013;33:1289–99. doi:10.1016/j.msec.2012.12.028.

11. Tamer M. Hamdy. Polymers and Ceramics Biomaterials in Orthopedics and Dentistry: A Review Article. Egypt J Chem 2018;61:620–30. doi:http://dx.doi.org/10.21608/ejchem.2018.3187.1273.

12. Kang BH, Ryu SC, Park HC. A study of the use of a hydroxyapatite and poly(methyl methacrylate) composite as a material for implants. J Ceram Process Res 2012;13:791–6.

13. Kang IG, Park C Il, Lee H, Kim HE, Lee SM. Hydroxyapatite microspheres as an additive to enhance radiopacity, biocompatibility, and osteoconductivity of poly(methyl methacrylate) bone cement. Materials (Basel) 2018;11. doi:10.3390/ma11020258.

14. Tamer M. Hamdy, Saniour SH, Sherief MA, Zaki DY. Effect of incorporation of 20 wt% Amorphous Nano-hydroxyapatite Fillers in Poly methyl methacrylate Composite on the Compressive Strength. RJPBCS 2015;6:975–8585. doi:10.1016/j.ijbiomac.2014.12.021.

15. Bistolfi A, Massazza G, Verné E, Massè A, Deledda D, Ferraris S, et al. Antibiotic-Loaded Cement in Orthopedic Surgery: A Review. ISRN Orthop 2011;2011:1–8. doi:10.5402/2011/290851.

16. Hanna A, khorshed lobna, El-Beih A, Sherief M, El Khashen A, Bassyouni G. Synthesis, Bioactivity, and Antimicrobial Studies on Zinc Oxide Incorporated Into Nanohydroxyapatite. Egypt J Chem 2019;0:0–0. doi:10.21608/ejchem.2019.12988.1812.

17. Iconaru SL, Motelica-Heino M, Predoi D. Study on europium-doped hydroxyapatite nanoparticles by fourier transform infrared spectroscopy and their antimicrobial properties. J Spectrosc 2013;1. doi:10.1155/2013/284285.

18. Bozkurt Y, Pazarlioglu S, Gokce H, Gurler I, Salman S. Hydroxyapatite lanthanum oxide composites. Acta Phys. Pol. A, vol. 127, 2015, p. 1407–9. doi:10.12693/APhysPolA.127.1407.

19. Ciobanu CS, Popa CL, Predoi D. Cerium-doped hydroxyapatite nanoparticles synthesized by the co-precipitation method. J Serbian Chem Soc 2016;81:433–46. doi:10.2298/JSC150824007C.

20. Hanna AA, Mousa SM, Sherief MA, Elkomy GM. Synthesis and characterization of nano-sized hydroxyapatite and doped with some rare earth elements from phosphogypsum waste. Int J ChemTech Res 2016;9:514–23.

21. Bauer AW, Kirby WM, Sherris JC, Turck M. Antibiotic susceptibility testing by a standardized single disk method. Am J Clin Pathol 1966;45:493–6.

22. Astm. Standard specification for acrylic bone cement. ASTM Int 2010:DOI: 10.1520/F451-08. doi:10.1520/F0451-08.2.

23. Pahlevanzadeh F, Bakhsheshi-Rad HR, Hamzah E. In-vitro biocompatibility, bioactivity, and mechanical strength of PMMA-PCL polymer containing fluorapatite and graphene oxide bone cements. J Mech Behav Biomed Mater 2018;82:257–67. doi:10.1016/j.jmbbm.2018.03.016.

24. Ghomi H, Fathi MH, Edris H. Effect of the composition of hydroxyapatite/bioactive glass nanocomposite foams on their bioactivity and mechanical properties. Mater Res Bull 2012;47:3523–32. doi:10.1016/J.MATERRESBULL.2012.06.066.

25. Panichev AM. Rare Earth Elements: Review of Medical and Biological Properties and Their Abundance in the Rock Materials and Mineralized Spring Waters in the Context of Animal and Human Geophagia Reasons Evaluation. Achiev Life Sci 2015;9:95–103. doi:10.1016/J.ALS.2015.12.001.

26. Lantanida U. Incorporation of Lanthanides in Human Dental Enamel 1996.

27. Zhou Y, Li N, Wang H, Yan J, Liu W, Xu S. Effects of the rare earth element lanthanum on the metal-ceramic bond strength of dental casting Co-Cr alloys. J Prosthet Dent 2019. doi:10.1016/J.PROSDENT.2018.08.017.

28. Ramenzoni LL, Weber FE, Attin T, Schmidlin PR. Cerium chloride application promoteswound healing and cell proliferation in human foreskin fibroblasts. Materials (Basel) 2017;10. doi:10.3390/ma10060573.

29. Xiang J, Li J, He J, Tang X, Dou C, Cao Z, et al. Cerium Oxide Nanoparticle Modified Scaffold Interface Enhances Vascularization of Bone Grafts by Activating Calcium Channel of Mesenchymal Stem Cells. ACS Appl Mater Interfaces 2016;8:4489–99. doi:10.1021/acsami.6b00158.

30. Kalyanaraman V, Naveen SV, Mohana N, Balaje RM, Navaneethakrishnan KR, Brabu B, et al. Biocompatibility studies on cerium oxide nanoparticles – combined study for local effects, systemic toxicity and genotoxicity *via* implantation route. Toxicol Res (Camb) 2019;8:25–37. doi:10.1039/C8TX00248G.

31. Roulet JF, Salchow B, Wald M. Margin analysis of posterior composites in vivo. Dent Mater 1991;7:44–9. doi:10.1016/0109-5641(91)90026-U.

32. Wright JA, Nair SP. Interaction of staphylococci with bone. Int J Med Microbiol 2010;300:193–204. doi:10.1016/j.ijmm.2009.10.003.

33. Serbetci K, Korkusuz F, Hasirci N. Thermal and mechanical properties of hydroxyapatite impregnated acrylic bone cements. Polym Test 2004;23:145–55. doi:10.1016/S0142-9418(03)00073-4.

34. Dalia Y. Zaki, Mohamed H. Zaazou, Maram E. Khallaf TMH. In Vivo Comparative Evaluation of Periapical Healing in Response to a Calcium Silicate and Calcium Hydroxide Based Endodontic Sealers the Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0). Open Access Maced J Med Sci 2018;6:1–5. doi:10.3889/oamjms.2018.293.

35. Zhang Q, Chen J, Feng J, Cao Y, Deng C, Zhang X. Dissolution and mineralization behaviors of HA coatings. Biomaterials 2003;24:4741–8. doi:10.1016/S0142-9612(03)00371-5.

36. Zhang L, Weir MD, Chow LC, Antonucci JM, Chen J, Xu HHK. Novel rechargeable calcium phosphate dental nanocomposite. Dent Mater 2016;32:285–93. doi:10.1016/j.dental.2015.11.015.

37. O'Donnell JNR, Skrtic D, Antonucci JM. Amorphous calcium phosphate composites with improved mechanical properties. J Bioact Compat Polym 2006;21:169–84. doi:10.1177/0883911506064476.

38. Zhao H, He W, Wang Y, Yue Y, Gao X, Li Z, et al. Biomineralizing synthesis of mesoporous hydroxyapatite-calcium pyrophosphate polycrystal using ovalbumin as biosurfactant. Mater Chem Phys 2008;111:265–70. doi:10.1016/j.matchemphys.2008.04.002.

39. Shahzad K, Mushtaq S, Akhtar S, Yaseen K, Amin F, Ali Z. Effect of lanthanum substitution on shape and cytotoxicity of zinc oxide (La x Zn 1-X O) nano-colloids. Mater Res Express 2019;6. doi:10.1088/2053-1591/ab024e.

40. Ducheyne P, Radin S, King L. The effect of calcium phosphate ceramic composition and structure onin vitro behavior. I. Dissolution. J Biomed Mater Res 2004. doi:10.1002/jbm.820270105.

تأثير دمج الهيدروكسي اباتيت المنشط باللانثانوم و السيريم على أسمنت العظم الراتنجي المُنتج من نفايات فوسفات الجبس

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توضح هذه الدراسة إستخدام نفايات فوسفات الجبس لتحضير هيدروكسي اباتيت وهيدروكسي اباتيت المنشط باللانثانم وهيدروكسيباتيت المنشط بالسيريوم. تم تحضير المنشطات المعتمدة على العناصر الأرضية النادرة بثلاثة تركيزات (0.25 ، 0.5 ، 0.75٪ من الوزن على التوالي) لاستخدامها كمالئات من جزيئات متناهية الصغر لتعزيز النشاط المضاد للبكتيريا ، الخواص الميكانيكية و التنشيط الحيوي لأسمنت العظام الراتنجي .تم تحضير المالئات من جسيمات نانوية و دمجها يدويًا بنسبة 20 ٪ بالوزن مع أسمنت العظم الراتنجي للحصول على خليط من مركبات الأسمنت بولى ميثيل ميثا اكريلات. أظهرت النتائج أن الاسمنت المحضر من الهيدروكسي اباتيت المنشط بالسيريوم بنسبة 0.5٪ من الوزن مع بولى ميثيل ميثا اكريلات يسمح بزيادة ملحوظة في النشاط المضاد للجراثيم ضد المكورات العنقودية الذهبية ، مع الحفاظ على قوة ضغط كافية ، كما أظهرت النتائج القدرة على إطلاق نسبة عالية من أيونات الكالسيوم و الفوسفور ، مما يشير إلى فرصة جيدة للمركب المبتكر فى تطبيقات طب الأسنان وطب العظام.