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Effect of incorporation of 20 wt% Amorphous Nano-hydroxyapatite Fillers in Poly methyl methacrylate Composite on the Compressive Strength.

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ABSTRACT

The purpose of this study was to prepare amorphous nano-hydroxyapatite fillers by sol-gel method and incorporating the prepared fillers into traditional PMMA bone cement to test the compressive strength of amorphous nHA/PMMA composite. The prepared fillers were characterized by XRD, FT-IR and TEM. We prepared composite specimens containing 20 wt% amorphous nHA in PMMA, then tested their compressive strength using universal testing machine. This experiment proved that the mechanical property of the prepared novel composites is satisfactory to be used as bioactive bone filler material. In particular, the 20 wt% nHA composite can be used as bioactive bone filler alternative to traditional PMMA

Keywords: Hydroxyapatite, PMMA, Bioactivity, Compressive strength, Bone filler, Bone cement.

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INTRODUCTION

Polymethyl Methacrylate (PMMA) cements were developed in the early 1960s and they have been classified as bioinert materials due to little formation of fibroblastic cells at the cement–bone interface. PMMA cement act as space filler material that provide mechanical support and chance for direct bone healing. In extreme cases due to lack of bioactivity, incomplete bone healing may be occurs. Even though PMMA has good mechanical properties and handling characteristics, their bioactivity is poor. In order to enhance its healing properties of affected bone, scientists have developed methods to enhance the bioactivity of traditional PMMA bone cement [1].

Biomaterials are a class of engineering materials has seen great advance in the modern dentistry. Among the different classes of biomaterials, bioceramic is one of the talented classes used as human bone filling materials serving for bone replacements, reconstructions and regenerations for long term durability without any hostile effect [2].

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] (HA) is an inorganic bioceramic compound which is widely used for various biomedical applications such as a bone substitute material in orthopedics and dentistry due to its strong mechanical properties, excellent biocompatibility, bioactivity and osteoconductivity. However, the crucial problem is their poor bioactivity [3].

Nano-hydroxyapatite (nHA) is a unique bioceramic novel material with a chemical composition and structure that mimics natural bone minerals. It is highly bioactive, biocompatible and provides excellent chemical bonding with natural bone [4]. The degradation rates of amorphous HA are higher than crystalline structure, which serve it as bioactive and biodegradable ceramics [5]. Sol-gel technique could be used for synthesizing nHA powder with the advantages of using easily obtainable and comparatively cheaper raw material together with the simplicity of experimental technique [5].

The mechanical properties of the bone cement are imperative for their success since it functions to fill the defected bone space components in the bony skeleton and to transmit loads through the surrounding bones and muscles. The bone cement is exposed to great mechanical stress in the body. In jaws, the biomechanical situation is rather complex due to effect of occlusion forces, involving different types of loading (bending, compression, and shear). According to ASTM F451-99 [6] and the international standard ISO 5833:2002 [7], the compressive strength should be fulfil a minimum of 70 MPa.

The purpose of this study was to prepare a novel nano-sized amorphous HA powder by a simple sol-gel technique to be added to conventional PMMA in 20 wt% without compromising its compressive strength. Several methods has been described for preparation of HA include precipitation, hydrothermal, hydrolysis, mechano-chemical and sol-gel. These techniques can create nano to micro sized HA. However, sol-gel method offers high product purity, homogeneous composition, and low synthesis temperature of the resulting HA to a significant extent, in comparison with above conventional techniques. In addition, the high reactivity of the sol-gel powders results in the decrease of the calcining and sintering temperatures [5].

MATERIALS AND METHODS

Synthesis of Hydroxyapatite Powder

The calcium phosphate (CaP) powders were prepared by the sol-gel method. Calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] (Merck, UK), ammonia solution (El-Nasr Pharmaceutical Chemicals, Egypt) and phosphoric acid solution (Burdick & Jackson, Germany) were used as starting precursors [5]. The molar concentrations of calcium nitrate tetrahydrate and di-ammonium hydrogen orthophosphate were adjusted so to obtain a theoretical Ca/P ratio of 1.67. The pH of the reaction mixture was adjusted by drop wise addition of di-ammonium hydrogen orthophosphate in to calcium nitrate tetrahydrate solution. The preparation was carried out under continuous stirring at 37 °C for 1 hour followed by ageing for about 24 hours. The precipitate was separated from its solution using a centrifuge (Sigma laboratory centrifuge, Germany). The white precipitate was washed with double distilled water, dried and finally sintered at 65 °C for 2 hours [8].

Characterization of Synthesized Hydroxyapatite Powder

The prepared powder was identified by X-ray Diffraction (XRD) (Siemens-Brucker D5000 diffractometer) with voltage and current settings of 40 kV and 40 mA, respectively, and Cu-K α radiation (1.540600 Å). The obtained XRD patterns were interpreted by comparing with model patterns on the JCPD databases. The present functional groups were confirmed by Fourier Transform Infrared (FT-IR) Spectroscopy (JASCO FT/IR-4100 spectrometer, Japan). A transmittance mode spectrum was taken in the wave number range 400-4000 cm⁻¹, using translucent pellets prepared by mixing powder sample with KBr. The particles size and morphology of the synthesized powders were evaluated using Transmission electron microscopy (TEM) (JEOL JEM-2100 HR TEM, Japan), at accelerating voltage of 200 kV with magnetic imaging resolution: 22 Å.

Preparation of nHA/PMMA Composite

The prepared nHA and PMMA (Cemex® Isoplastic, Tecres, Italy) were manually mixed to give a composite. The weight percentage of nHA was 20%. The control groups were contained PMMA only without fillers. The ingredients were manually blended until an appropriate mix was obtained. Once the mix reached the dough stage, the composite was packed into the stainless steel perforated mould designed with internal dimensions of 6 mm in diameter and 12 mm in height, supported from both sides by metal plates [6].

Measurement of Compressive Strength of the Prepared nHA/PMMA Composite

Five cylindrical specimens of 12 mm in high and 6 mm in diameter for each group were prepared according to standard specification for acrylic bone cement specified in the ASTM F-451-99 standard [6] (Figure 1).



Figure 1: Metallic mould used for compressive strength testing

After setting, specimens were removed and ground on silicon carbide papers ranging from 650 to 2000. Specimens were inspected visually for discontinuity, voids, cracks and irregularities in ambient light and if present the specimens were discarded.

All specimens mounted universal testing machine (Model LRX-Plus; Lloyd Instruments Ltd., Fareham, United Kingdom) at a crosshead speed of 20 mm/min with a load cell of 5 kN. The specimens were statically loaded in compression manner using. Data were recorded using computer software (Nexygen-MT; Lloyd Instruments Ltd., Fareham, United Kingdom). The maximum failure load was recorded and the compressive strength was calculated from the recorded peak load.

RESULTS AND DISCUSSION

The XRD pattern revealed hexagonal phase peaks (at 2 $^{\circ}$ theta angles: 32.038 $^{\circ}$) corresponding to hydroxyapatite, Ca₅(PO₄)₃(OH) (JCPDS card 86-0740) (Figure 2)[9]. Absence of characteristic peaks of secondary phases was noted, indicating that the final product was of high purity. Moreover, the particles showed a highly amorphous structure. Such anticipated high solubility in aqueous environment would encourage the release of calcium and phosphate ions in aqueous environments and lead to deposition of

apatite mineral. Nano-sized particles with size range from 3-10 nm were obtained which is very suitable for biomedical application.

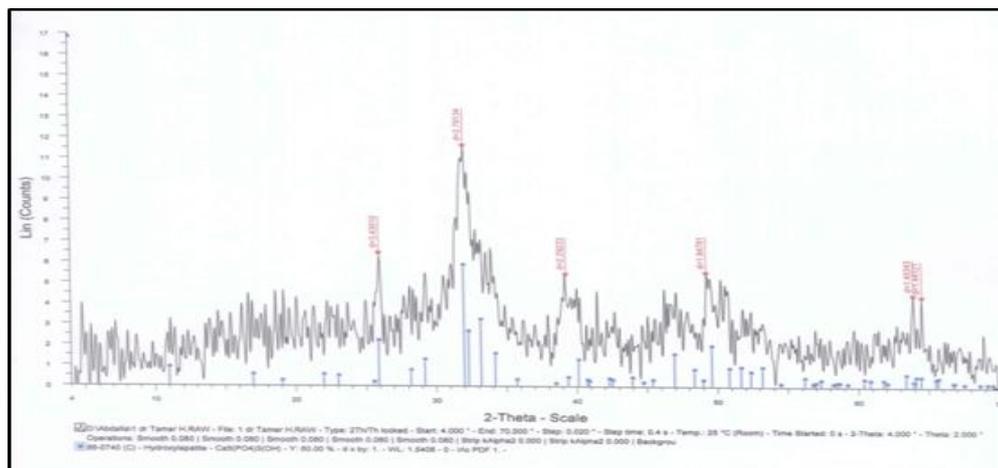


Figure 2: XRD pattern of the prepared CaP powders

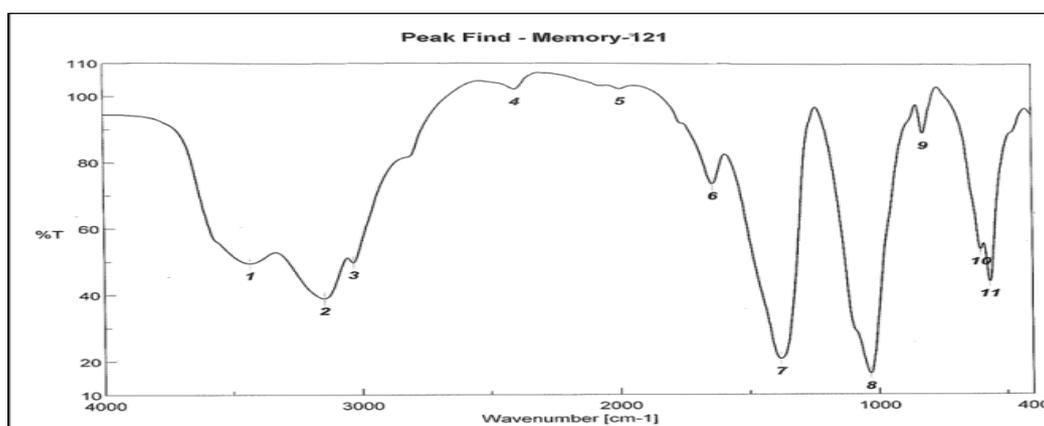


Figure 3: FTIR spectra of the prepared CaP powders

The FTIR spectra confirmed the characteristic absorption peaks corresponding to HA particles (Figure 3)[10]. The broad band at 3432.67 cm^{-1} was corresponding to adsorbed water, while band at 1639.2 cm^{-1} represent stretching mode of the O-H. The bands at 823.455 and 1034.62 cm^{-1} were the stretching mode of PO_4^{3-} group. The sharp peaks at 566.005 and 601.682 cm^{-1} represent the vibration peaks of PO_4^{3-} . The band that appears at 1380.78 cm^{-1} may correspond to CO_3^{2-} from carbon dioxide formed during preparation from air.

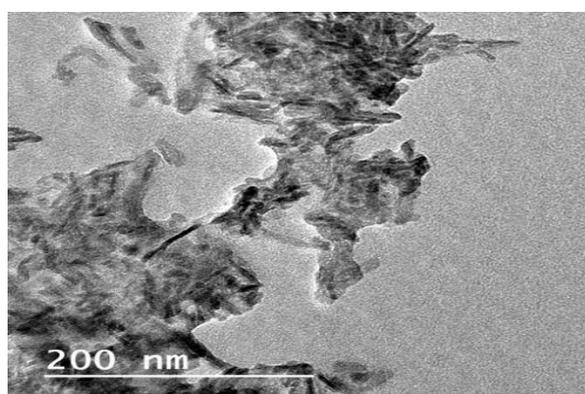


Figure 4: TEM micrographs of the prepared CaP powders

The TEM analysis results revealed rod-like shape particles, which could be appropriate for alignment within polymer matrices. The particles size range lower than 10 nm without crystallinity (Figure 4) thus confirming the results by XRD. Certain agglomeration of particles was observed which may be attributed to the large surface area and energy associated with nanoparticles.

Control group showed a higher statistically significantly mean compressive strength value compared to 20% filler group, as shown in Table 1 (Figure 6). In general, both groups exceeded the minimum requirements of 70 MPa according to ASTM F451-99 [6] and ISO 5833:2002 [7]. Although 20% nHA filler not silanized yet it did not impair the mechanical requirement.

Table 1:The mean \pm standard deviation (SD) values and results of one-way ANOVA and Tukey’s post-hoc tests for comparison between compressive strength values of the two groups.

Control mean (SD)	20% Filler mean (SD)	P-value
95.1 (3.9) ^a	82.6 (2.1) ^b	<0.001*

*Different letter within each row are significant different at $P \leq 0.05$

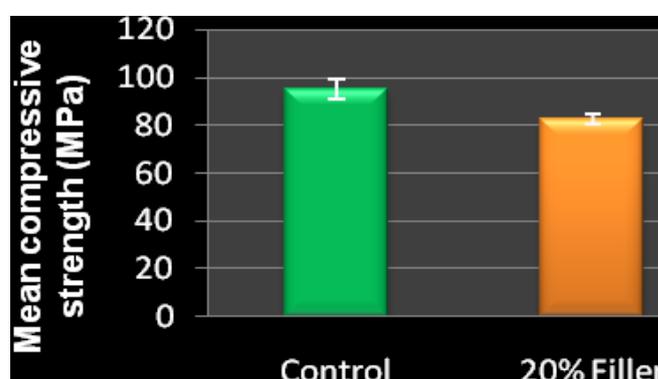


Figure 5: Bar chart showing the mean compressive strength values of the two groups

CONCLUSIONS

The compressive strength of the 20 wt% nHA in PMMA composites were about 82.6 MPa, Which considered as a good mechanical strength according to ISO 5833:2002 and ASTM F451-99. These composites have accepted mechanical properties to be used as novel bioactive bone filler material alternative to traditional PMMA. Further studies of the bioactivity of the prepared composite were needed.

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