



# INVESTIGATION OF MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HYBRID BONE CEMENTS

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## ABSTRACT

This study investigates the influence of incorporating bioactive ceramic particles on the mechanical performance of acrylic bone cement. The formulated composites contain certain weight fractions of hydroxyapatite (3,8,16) wt%, magnesia (2,3.5,5) wt% and a fixed amount of titania (2 wt%). Vacuum mixing technique was adopted in order to reduce porosity and stress concentration. The microstructure of fabricated composites was characterized through Scanning Electron Microscopy (SEM) and the mechanical properties were evaluated through tensile and microhardness tests. Results showed deterioration in tensile strength with increasing amount of fillers which is attributable to the agglomeration of reinforcement phase which represented weak points in the matrix for crack initiation and propagation. Moreover, the strength results are consistent with the SEM images that showed significantly increased agglomerates with increasing amount of fillers. Results showed an enhancement in modulus of elasticity with the incorporation of strong fillers. However, the results of microhardness test did not reveal significant changes, where hardness can be affected by content of residual monomer, porosity and other material properties in addition to composition.

**Keywords:** PMMA, hydroxyapatite, vacuum mixing, MgO, hardness.

## 1. INTRODUCTION

For many years, bone cements have been utilized successfully in anchoring metallic implants to the bone in total joint replacement surgeries, also they serve as a filling material for bone defects and procedures such as vertebroplasty and kyphoplasty. The most widely used bone cement is polymethylmethacrylate (PMMA). The influence of cement mixing techniques on the quality have been mentioned before [1-4]. Porosity in PMMA is shown to be reduced by vacuum-mixing [5, 6], accompanied by an enhancement in mechanical properties [7-9]. Mainly, application of bone cements in TJR involves transferring stresses from prostheses to the bone and increasing the capability tolerating loads that is provoked by surgery structure. Induced stresses are responsible for causing cement fractures and creating debris in interfaces, leading to bone degradation and eventual recurrence of replacement surgery.

Aiming for the augmentation of mechanical and physicochemical characteristics of bone cements, researchers have examined the influence of various materials on cement properties. As found naturally in bone, hydroxyapatite (HA), is the most frequently used bioceramic in orthopedics. HA is bioactive and thus, it encourages bone growth into available porosities, as the physico-chemical action involving HA and bone tissue conveys mechanical firmness. These bonds allow stress transfer, prohibiting fractures at the cement/bone interfaces. Addition of HA to PMMA has been reported to augment the compatibility and osteoblast reaction through direct encouragement of osseointegration [10-13].

In addition to HA, there is a significant appeal for Titania, as a result of its many benefits as a biomedical material. Moreover, TiO<sub>2</sub> is costly effective, chemically and thermally stable with good optical features. TiO<sub>2</sub> is proven to be a bioactive material by numerous studies

presenting strong interfacial bonds with bone tissue [14-17].

It is reported large amounts of titanium dioxide powder (50-60 wt%) limits the handling characteristics of bone cement [15]. With increasing amount of hard additives, the visco-elasticity is probable to drop, turning the cement brittle. decreased visco-elasticity can lead to high occurrence of cement fracture along with poor results clinically.

Magnesia (MgO) is another bioactive material and suitable additive to PMMA, as osteoblasts adhesion to the cement containing magnesium oxide was considerably higher than the adhesion to the PMMA alone ( $P < 0.001$ ) with no considerable changes in mechanical strength [18].

The objective of this present study was to investigate the incorporation of HA; MgO and TiO<sub>2</sub> particles into PMMA bone cement with a contemporary cement mixing technique. The mechanical properties of the resultant hybrid cements were characterized.

## 2. MATERIALS AND METHODS

Self cure acrylic powder (Spofadental) and methylmethacrylate (spofadental) were used for production of Polymethylmethacrylate (PMMA) as the polymeric matrix of composite. Hydroxyapatite micro powder was purchased from Sunkoo Chemical Ltd. has a white fine powder of  $d_{90} = 16.6 \mu\text{m}$ , 51.4-54.0 CaO%, 6-8 PH and max. Moisture % of 3%. Titanium oxide (EV Nano Technology Co., Ltd) of 99.9% and  $d_{90} = 35.63 \mu\text{m}$ . Magnesium oxide powder (Sky Spring Nanomaterials, Inc. USA) have a polyhedral morphology with a 99.5% purity and ( $< 50 \mu\text{m}$ ) APS were used as reinforcement phase. The cement powder composition is (MMA+MA) while the liquid part is composed of (methylmethacrylate, dimethylparatoluidine, ethylene glycoldimethacrylate). In order to avoid air bubbles that induce stress concentration and cracks initiation in the sample, reduce porosity and



consequently improve mechanical performance, vacuum mixing technique was adopted to prepare the samples. For the cement dough preparation, weighed amounts of PMMA, HA, TiO<sub>2</sub> and MgO powders were first homogenously mixed for 30 minutes followed by addition of liquid monomer and mixing with vacuum pressure

reaching 18 bar for 1 minute. The weight ratio of powder to liquid components is 2:1. After mixing, the cement dough was molded using compression molding method and kept for 10 minutes, then the hardened sample was ejected from the mold. The composition of the samples are shown in Table-1.

**Table-1.** Weight percentages of TiO<sub>2</sub>, HA and MgO bioactive particles in PMMA composites.

PMMA	TiO <sub>2</sub> wt%	HA wt%	MgO wt%	Notation
2:1 powder to liquid	2	3	2	M1
			3.5	M2
			5	M3
		8	2	M4
			3.5	M5
			5	M6
		16	2	M7
			3.5	M8
			5	M9

Microstructure, tensile and microhardness inspections have been performed in order to evaluate the properties of manufactured PMMA composites. The microstructure of fabricated cements was characterized using scanning electron microscopy (SEM) (FEI, INSPECT S 50). All specimens were applied to polishing and grinding before testing. For tensile, six specimens for each group were fabricated according to ASTM D 638 with dimensions of 3.2\*12\*57 mm [19]. Test was done using testometric device as shown in figure 1 with a maximum testing force of 50 KN and the head speed used was 1 mm/min.



**Figure-1.** Tensile specimen during testing.

Hardness test was carried out on samples having a thickness of minimum 3 mm. A load of 100 grams (0.98N) HV1 was applied for 10 seconds. 3 indentations as in Figure-2 were taken for each specimen and the average value represented the hardness.

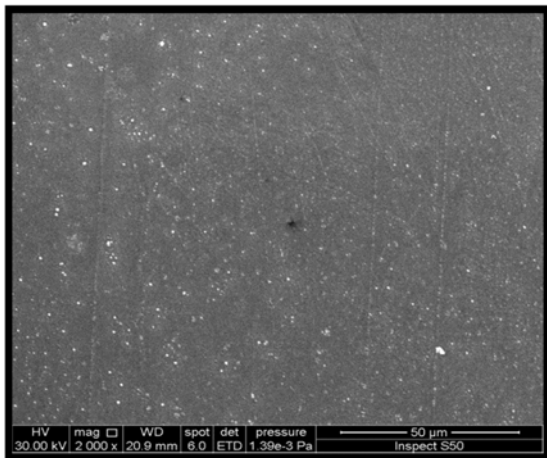


**Figure-2.** Hardness indentation made on the surface of one specimen.

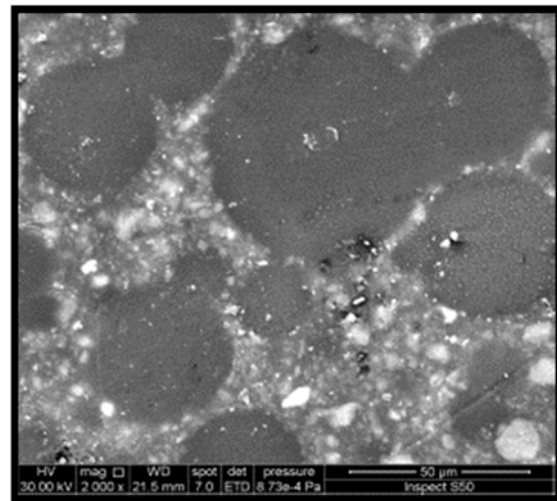
### 3. RESULTS AND DISCUSSIONS

#### 3.1 Microstructure characterization

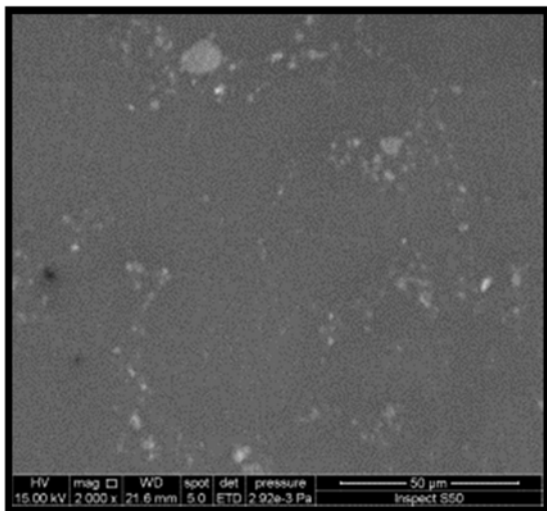
The spreading of additives in the polymer matrix is considered as a major factor affecting the improvements of composite material, which must attain homogeneous or uniform fillers dispersion in order to modify the physical and mechanical features. The microstructures of pure bone cement and the distribution of additives in resultant hybrid composites were observed through the SEM images shown in Figures 3-6.



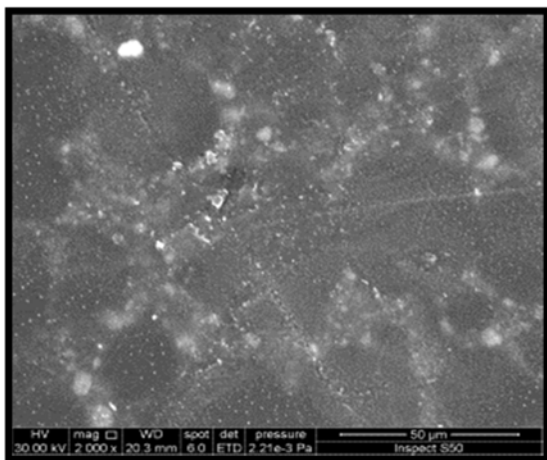
**Figure-3.** SEM image of pure PMMA.



**Figure-6.** SEM image of PMMA containing (2%wt TiO<sub>2</sub>+16wt% HA+5wt% MgO).



**Figure-4.** SEM image of PMMA containing (2%wt TiO<sub>2</sub>+3wt% HA+2wt% MgO).



**Figure-5.** SEM image of PMMA containing (2%wt TiO<sub>2</sub>+8wt% HA+3.5wt% MgO).

Slight agglomerations of filler materials can be observed with the relatively small additions, mostly with 3wt% HA cements (M1). With higher concentrations of HA, the distribution of inorganic phase in the matrix where precipitates are closely spaced so forming a semi-continuous network along grain boundaries. It can be clearly seen with increasing amount of ceramic fillers that these particles are located in the grain boundaries of PMMA as the irregular atoms arrangement at grain boundary provides lower atomic packing and high energy. Atoms are thus able to spread more rapidly to form precipitates. This high energy makes the grain boundary more "chemically reactive" than the grain itself, therefore, boundaries are an ideal position for both nucleating and growth of precipitates.

### 3.2 Tensile test

The ultimate tensile strength as well as modulus of elasticity of pure bone cement and composites were determined through tensile test by evaluating the influence of incorporating bioactive ceramics on this property as shown in Table-2.

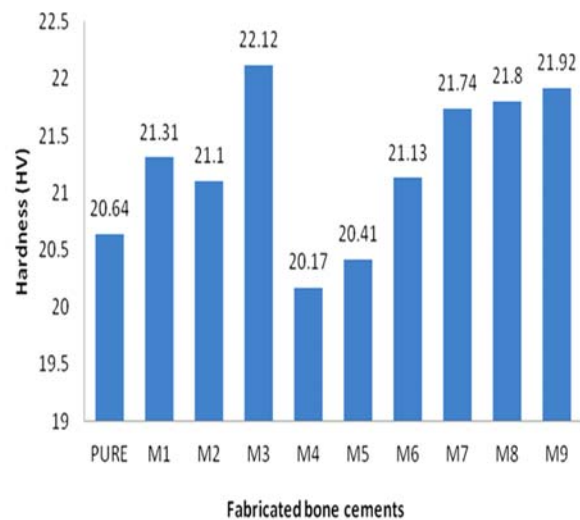
**Table-2.** Tensile properties of micro bioactive hybrid composites.

Fabricated formulation	UTS (MPa)	E (GPa)
Pure PMMA	29.73	1.56
M1	29	1.48
M2	25.59	1.64
M3	22.49	1.71
M4	21.75	1.78
M5	23.65	1.9
M6	18.13	1.61
M7	21.65	1.7
M8	25.3	2.13
M9	18.96	1.99

The first composite which contained the least amount of fillers showed insignificant change in strength which indicated a homogenous distribution of (3wt%HA+2wt%MgO+2wt%TiO<sub>2</sub>). On the contrary, the introduction of higher amounts of ceramic particles increased the elastic modulus of bone cement and decreased the cement strength. However, same concentrations of magnesium oxide seem to show insignificant changes with relatively large concentrations of hydroxyapatite (8 and 16) %wt. This reduction in strength can be associated with the occurrence of defects in the cement-filler particles interface. Increased content of inorganic particles was also reported by Kim *et al.* to reduce cement strength [20]. The reduction in strength can be explained by the hybrid composite microstructure, which shows the reinforcement particles forming agglomerates. Particle agglomeration is likely to decrease the load resistance of the composite, even though the ceramic additives were strong enough to raise the modulus. Agglomerates constitute weak areas, so with load application and stress transfer to these weak areas, the bonds linking the agglomerated particles break and the stress is transferred back to matrix initiating cracks and stress concentrations and eventually leading to cement failure [21].

### 3.3 Hardness test

The hardness of hybrid composites experienced insignificant changes with respect to the pure bone cement. However, the highest value was recorded for bone cement with (2wt% TiO<sub>2</sub>+3wt% HA+5wt% MgO) with an enhancement of 7%. Also, 5wt% of magnesia showed the largest enhancement in Vickers hardness when compared to other weight fractions of MgO. Bearing in mind that hardness can be affected by several factors such as residual monomer content, material constitution, porosity, etc., it could be concluded that the examined modifications of PMMA bone cement did not yield substantial changes in the Vickers hardness. Figure-5 shows the variation of hardness value with the varying hybrid compositions.

**Figure-7.** Vickers hardness values of all fabricated bone cements.

## 4. CONCLUSIONS

The main points concluded from this work:

- Modulus of elasticity enhanced in the fabricated hybrid composites with the incorporation of strong fillers. However, as the amount of fillers increased, the tensile strength decreased as a result of particles agglomeration which represented weak points in the matrix for crack initiation and propagation.
- The strength results are consistent with the SEM images that showed significantly increased agglomerates with increasing amount of fillers.
- No significant changes were recorded in the Vickers hardness of bone cement.

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