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A study of the use of a hydroxyapatite and poly(methyl methacrylate) composite as a material for implants

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The purpose of this study was to identify a HAp/PMMA composite with ideal mechanical characteristics and bioactivity for use as an implant. We prepared composite samples containing either 0 wt%, 10 wt%, 20 wt%, 3 0wt% or 40 wt% HAp in PMMA, then tested their mechanical properties and analyzed the composite composition. This experiment proved that the mechanical properties and bioactivity of the composite can be satisfactory for use in an implant. In particular, the 10 wt% HAp composite can be a substitute for use in dental implants.

Key words: Hydroxyapatite, PMMA, Bioactivity, Mechanical Properties, Physical properties.

Introduction

Biological materials have seen great development in the 21st century. Inorganic biomedical materials research and applications have been very important to these advances. In particular, hydroxyapatite (HAp) is a unique, surface active material with its chemical composition and structure similar to natural bone[1-2]. HAp has good bioactivity and biocompatibility[4-6] and there is no implantation rejection from human tissue. It provides excellent chemical bonding with natural bone and is used as a bone cement. Even though HAp has good bioactivity, the mechanical strength is poor [7]. The mechanical properties of HAp limit its applications. In order to enhance its mechanical properties, scientists have developed various methods to make different types of HAp composites.

Some experiments produced an evaluation of the characteristics of a poly methyl methacrylate (PMMA) [8-10] and HAp [11-13] composites with the intention of designing a replacement for titanium as a material in implants. PMMA has been widely used as a biomaterial in dentistry, orthopedic retainers and as bone cement, and it has strong mechanical properties. However, the primary problem with PMMA is poor bioactivity. In our design, we used HAp to enhance the mechanical properties of PMMA, in a composite form. The mechanical properties of the PMMA/HAp composites were compromised by material incompatibility between the PMMA and HAp. Modification of the PMMA/HAp composite was required in order to achieve a high performance base material with better mechanical properties. Use of a polymeric compatibilizer and coupling agent can improve the interaction and adhesion between the organic PMMA matrix and inorganic HAp particles.

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Experimental

HAp powder (≥ 98% purity) which was filtered through a 325-mesh (≥ 45 μm) sieve was considerately supplied by Bone Tech Inc. (Korea) and used without further purification. The properties of the HAp powder were characterized by powder X-ray diffraction (XRD, Miniflex II, Rigaku, Co. Ltd., Tokyo, Japan), and energy-dispersive X-ray spectroscopy (EDS, JEM-2011, Jeol Ltd., Tokyo, Japan). Figure 1 provides the XRD patterns and Table 1 provides the EDS profile produced from the HAp powder. The PMMA beads (≥ 99.9% purity) were considerately supplied by LG MMA Corp. (Korea) and used without further purification. Additional characteristics of the PMMA beads can be found in their Material Safety Data Sheet (MSDS).

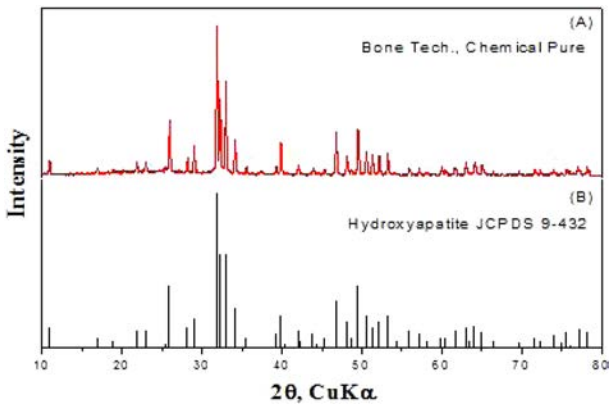

Fig. 1. XRD patterns produced from the HAp powder: (A) prepared HAp and (B) standard peak of HAp provided by JCPDS.

Table 1. EDS profile of HAp powder.

Element	Atomic%
O	69.25
P	11.50
Ca	19.25
Totals	100.00
Ca/P	1.674

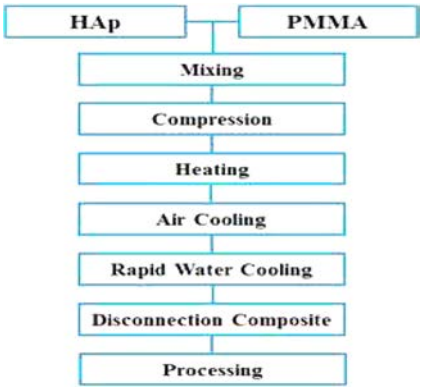

Fig. 2. Processing of the of PMMA/HAp composites.

Manufacture of the PMMA/HAp composite

In this experiment, we mixed the HAp (BoneTech Inc., purity 98%) and PMMA (LG MMA Corp., purity 99.9%) to make composites in different percentages. The weight percentage of HAp in each composite was in the range of 0% to 40%. The ingredients were mixed using a centrifuge until appropriately balanced. The mixture was then put into a mold and an oil-hydraulic pressure of 196.133 MPa was applied. Then, we heated the mixture to 200°C for 30 minutes, then let it cool in ambient air for 10 minute, followed by a final water cooling step. We observed that at high temperature the PMMA swells, so it is important to use a fixed mold.

Figure 2 shows a schematic flowchart describing the experimental procedure for preparing the PMMA/HAp composites.

Physical strength test

Compressive strength test

According to standard (KS P ISO 13779-1), the diameter of the sample was fabricated to be 8 mm and the height, 16 mm. In order to decrease the error in the results, 4 samples were tested at each composite percentage.

Bending strength test

We used the three point bending test to evaluate the strength of the finished composites. The samples were fabricated according to the standard (KS M ISO 1209-1 ~ 1209-2) such that the length of the sample was greater than 30 mm, the height was 1.5 mm ± 0.2 mm, and the width was 2.5 mm ± 0.2. In order to decrease the error, we tested 4 samples of each composite percentage.

Tensile strength test

The samples were fabricated according to the standard (KS M ISO 527-1 ~ 527-5) such that the overall length of each was more than 30 mm, the distance between shoulders was 12 mm ± 0.5, the radius was more than 12 mm, the height was more than 2 mm, and gauge length was 10 mm ± 0.2. In order to decrease the error, 2 tests were made of each composite percentage.

Hardness test

We used the Vickers hardness test to examine the surface of each composite. In order to decrease the error, we tested 2 samples of each composite percentage.

Bioactivity test

The bioactive properties of the composite samples in SBF solution was tested at 6 and 12 weeks. The temperature of the samples in the SBF solution was maintained to be similar to that found in the human body (37 °C). After 6 and 12 weeks, we observed the sample surfaces using a field-emission scanning electron microscope (FE-SEM, HITACHI-S4700, HITACHI, Japan).

Cell proliferation test

Cell cultures

MC3T3-E1 murine preosteoblasts (subclone 14, obtained from the Chinese Academy Of Science Cell Bank and maintained in our research lab) were cultured in alpha-minimum essential medium (a-MEM), supple-mented with 10% (v/v) fetal bovine serum (FBS, Sigma) and 1% (v/v) penicillin/streptomycin (PS, Sigma). Each cell culture was carried out at 37 °C under 5% CO_2 in a humidified incubator, and the culture medium was changed every 2 or 3 days. When the cells reached 80% confluence, they were detached using 0.25% (w/v) of trypsin containing 0.02% (w/v) of ethylenediamine tetraacetic acid (EDTA) in a phosphate buffered saline (PBS) solution, and then seeded on a new tissue culture plate for subculture.

Cell proliferation

MC3T3-E1 cells were seeded on the PMMA/HAp composite surface under the same culture conditions described above at a density of 2×10^4 cells/well in a 48-well plate. The cell proliferation was estimated using a tetrazolium salt MTT method. At 14 days, the medium was changed and the cells were then incubated with MTT solution under normal culture conditions for 3 h. The solution was transferred to a 96-microwell plate and the absorbance of each well was measured using an ELISA Reader (Molecular Devices, USA) at 450 nm. The results were obtained from duplicate samples and data were presented as the mean ± SD.

Forming test

We made the implant samples using small machine tools, and as such, provided confirmation of the processability of the PMMA/HAp composites.

Results and Discussion

Manufacturing of the composites

This experiment used HAp powders and nontoxic PMMA beads to produce the composite. Mechanical processing was easy to apply to the composite material. However, after air cooling, the mold and composite remain hot and inseparable and the material may be destroyed when the mold is separated. Therefore, after air cooling we used water cooling to make it easy to separate the composite samples from their molds.

Strength test

This experiment used the Universal testing machine (UTM) to evaluate the strength of the composites. Figure 3 demonstrates that the compressive strength of these composites was approximately 178-381 MPa. Examination of figure 3 reveals that when the HAp content increased the compressive strength dropped. This was because even though polymers, in general, are made of compound chains which combine polymer and polymer sufficiently, HAp is a ceramic which does not combine as well with a polymer. The ceramic is relatively stiff and prevents the spread and movement of the polymer within the composite [14-16].

Figure 4 shows the results of the bending strength test, which revealed results of about 43-68 MPa. This result is the same as that seen for the compressive strength test, as the HAp content increased the bending strength decreased. The HAp combined weakly to the polymer chains, thus lowering the mechanical properties.

Figure 5 shows that the result of the tensile strength test was about 33-50 MPa. When the HAp content increased, the tensile strength and the modulus of elasticity decreased, a result of the weak polymer chain combinations due to the presence of HAp.

The Vickers hardness test of the surface of the composites, seen in figure 6, revealed the hardness to be about 22.9-33.3 HV. The hardness test data was different than other strength tests in that when the HAp content increased, the hardness value also increased. This is because HAp has a higher hardness than PMMA.

PMMA/HAp composite SBF activation test

We performed a SBF test for bioactivity of the PMMA/HAp composite. Figure 7 is the FE-SEM images

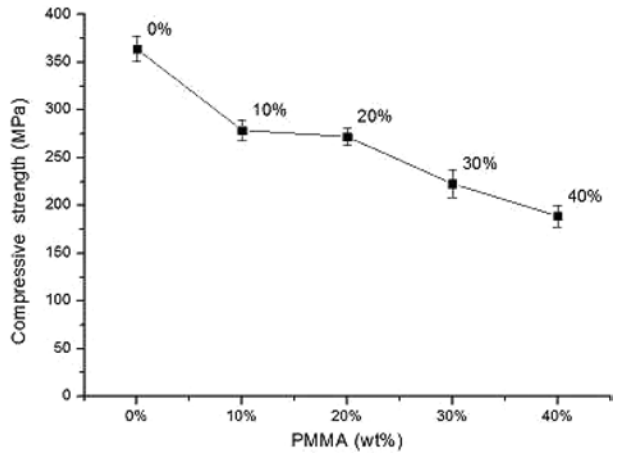

Fig. 3. Compressive strength of the PMMA/HAp composites.

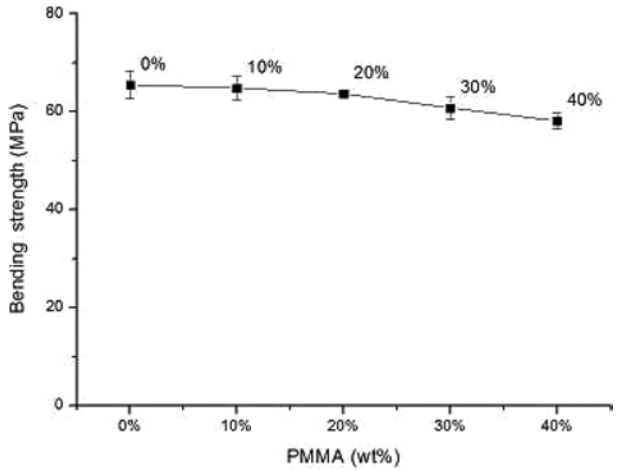

Fig. 4. Bending strength of the PMMA/HAp composites.

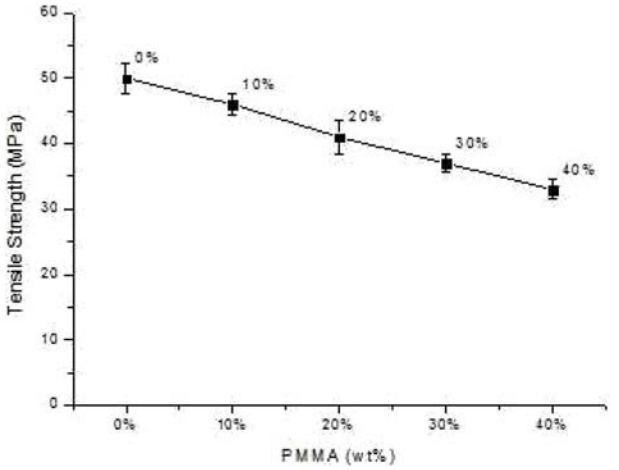

Fig. 5. Tensile strength of the PMMA/HAp composites.

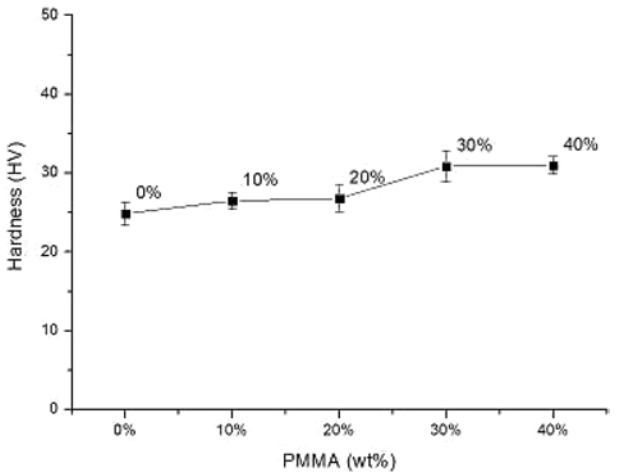

Fig. 6. Vickers hardness of the PMMA/HAp composites.

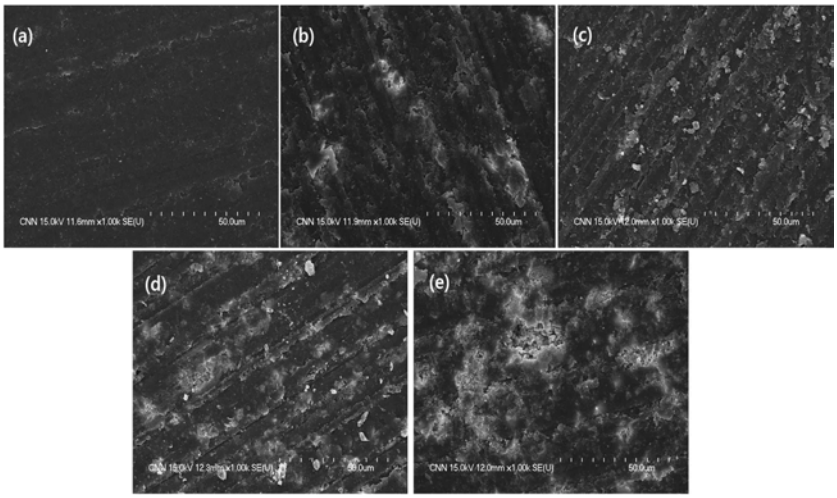

Fig. 7. The SEM images of the surface of the PMMA/HAp composites. (a): PMMA 100 wt%, (b): HAp 10 wt%, (c): HAp 20 wt%, (d): HAp 30 wt%, (e): HAp 40 wt%.

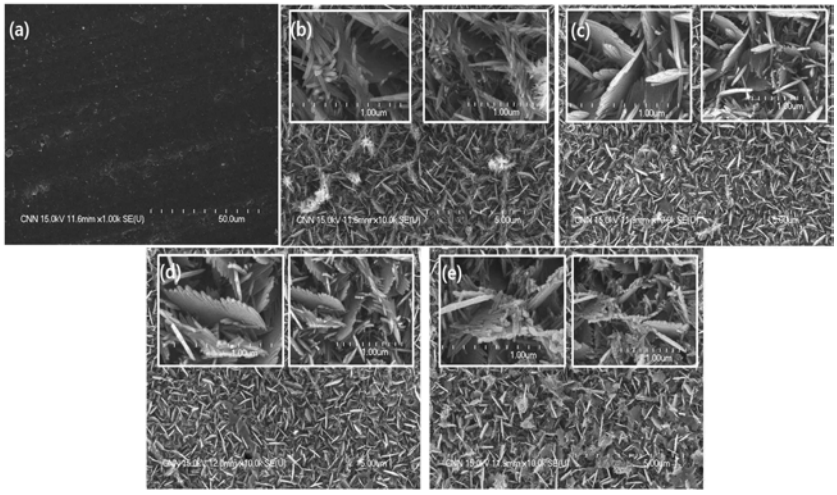

Fig. 8. The SEM images of PMMA/HAp composites (Reaction with SBF solution from 6 weeks). (a): PMMA 100 wt%, (b): HAp 10 wt%, (c): HAp 20 wt%, (d): HAp 30 wt%, (e): HAp 40 wt%.

Table 2. The EDX of PMMA/HAp composite (SBF solution before the reaction).

PMMA 100wt%

Element	Weight%	Atomic%
C K	64.62	70.87
O K	35.38	29.13
Totals	100.00	

HAp 10wt%

Element	Weight%	Atomic%
O K	48.28	67.85
P K	19.09	13.85
Ca K	32.63	18.30
Totals	100.00	

HAp 20wt%

Element	Weight%	Atomic%
O K	44.49	64.45
P K	20.28	15.17
Ca K	35.23	20.38
Totals	100.00	

HAp 30wt%

Element	Weight%	Atomic%
O K	43.60	63.77
P K	19.31	14.59
Ca K	37.08	21.65
Totals	100.00	

HAp 40wt%

Element	Weight%	Atomic%
O K	42.01	62.28
P K	19.56	14.98
Ca K	38.43	22.74
Totals	100.00	

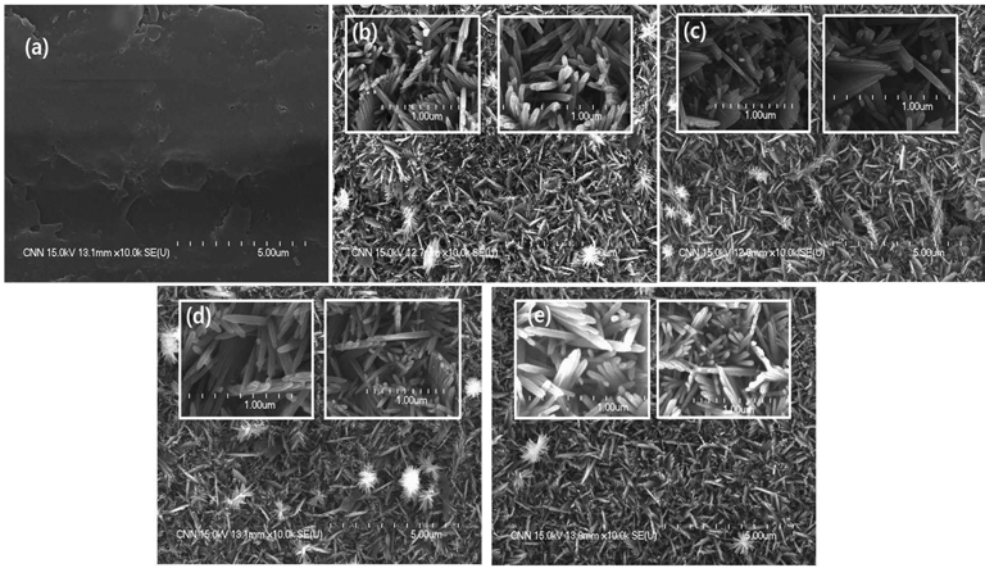

Fig. 9. The SEM images of PMMA/HAp composites (Reaction with SBF solution from 12 weeks). (a): PMMA 100 wt%, (b): HAp 10 wt%, (c): HAp 20 wt%, (d): HAp 30 wt%, (e): HAp 40 wt%.

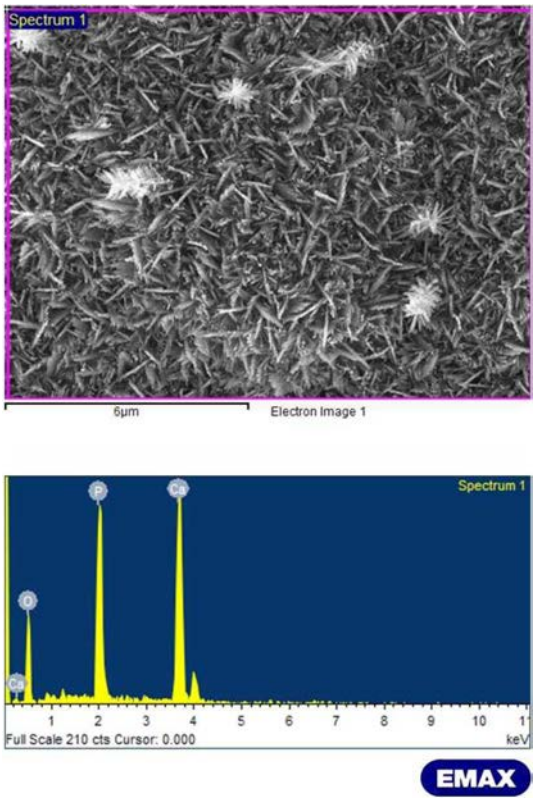

Fig. 10. The EDX spectra identifying Ca^{2+} ions resulting from HAp bioactivity in the composite containing 40 wt% of HAp.

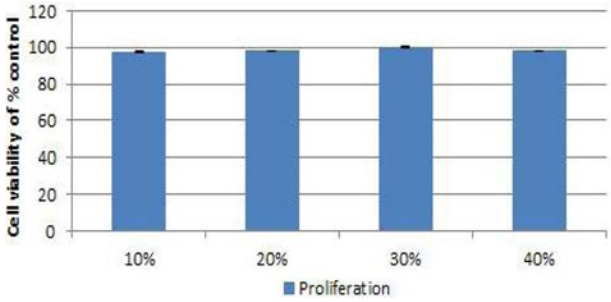

Fig 11. Proliferation of MC3T3-E1 as compared to HAp/PMMA ratio.

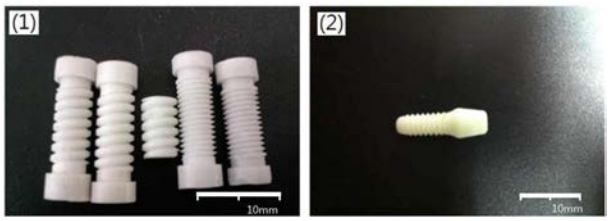

Fig. 12. The shapes of the PMMA/HAp composite as manufactured.

of the composite surface before the reaction with SBF. It shows an absence of bioactivity. Table 2 is the EDX of the PMMA/HAp composite. When the HAp content increased the atomic percent of Ca^{2+} also increased. Figure 8 shows the FE-SEM images of the samples after 6 weeks immersion. Figure 9 shows the FE-SEM image of the sample after 12 weeks immersion. These results indirectly prove that the PMMA/HAp samples would be bioactive in the human body. We assumed, on the basis of the increased concentration of Ca^{2+} ions observed, that reactions between the Ca^{2+} ions and HAp occurred at the sample surfaces. Bioactivity was apparent from 6 to 12 weeks. Figure 10 shows the EDX analysis revealing Ca^{2+} ions resulting from HAp bioactivity [17].

Cell proliferation test

Figure 11 shows the cell proliferation results for all the composites. The cells proliferate in the PMMA/HAp composites. Also each sample has about 100% cell viability. So we learned that the PMMA/HAp composites have a non-toxic and demonstrated excellent bioaffinity.

Manufacture of the composites

The composites were manufactured as illustrated in Figure 12. The pure HAp was difficult to manufacture because of its fragility, but the PMMA/HAp composites were easily manufactured and we could make many complex shapes.

Conclusions

In this study, we found that the compressive strength of the PMMA/HAp composites was about 178-381 MPa, the bending strength was about 43-68 MPa and the tensile strength was about 33-50 MPa. When the HAp content increased, the mechanical strength decreased but the hardness increased. This is because HAp has a higher hardness than PMMA. When the HAp was 0 wt% in the composite sample, the compressive strength was about 381 PMa, the bending strength was about 68 MPa, the tensile strength was about 50 MPa, and the Vickers hardness was about 50 HV. When the HAp was 10 wt% of the composite, the compressive strength was about 308 MPa, the bending strength was about 61 MPa, the tensile strength was about 46 MPa, and the Vickers strength was about 26.5 HV. In the PMMA without HAp, the sample strength was suitable and non-toxic, but there was no bioactivity. A 40 wt% PMMA/HAp composite had no toxicity and there was bioactivity, but the strength was weak. We found that a 10 wt% PMMA/HAp composite had a good mechanical strength and the necessary bioactivity that can be useful for making artificial bones and dental implants.

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