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ORIGINAL ARTICLE

Effects of hexagonal boron nitride on mechanical properties of bone cement (Polymethylmethacrylate)

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ABSTRACT

Objectives: The aim of this study was to investigate the effects of adding hexagonal boron nitride at four different concentrations to polymethylmethacrylate (PMMA) bone cement, which is commonly used in orthopedic surgeries, on the mechanical properties and microarchitecture of the bone cement.

Materials and methods: The study included an unaltered control group and groups containing four different concentrations (40 g of bone cement with 0.5 g, 1 g, 1.5 g, 2 g) of hexagonal boron nitride. The samples used for mechanical tests were prepared at 20±2°C in operating room conditions, using molds in accordance with the test standards. As a result of the tests, the pressure values at which the samples deformed were determined from the load-deformation graphs, and the megapascal (MPa) values at which the samples exhibited strength were calculated.

Results: The samples with 0.5 g boron added to the bone cement had significantly increased mechanical strength, particularly in the compression test. In the group where 2 g boron was added, it was noted that, compared to the other groups, the strength pressure decreased and the porosity increased. The porosity did not change particularly in the group where 0.5 g boron was added.

Conclusion: Our study results demonstrate that adding hexagonal boron nitride (HBN) to bone cement at a low concentration (0.5 g / 40 g PPMA) significantly increases the mechanical strength in terms of MPa (compression forces) without adversely affecting porosity. However, the incorporation of HBN at higher concentrations increases porosity, thereby compromising the biomechanical properties of the bone cement, as evidenced by the negative impact on compression and four-point bending tests. Boron-based products have gained increased utilization in the medical field, and HBN is emerging as a promising chemical compound, steadily growing in significance.

Keywords: Bone cements, boron, mechanical strength.

Research on various substances added to polymethylmethacrylate (PMMA) has contributed to the orthopedic literature. In addition to antibiotics, silver-containing nanoparticles have also shown promise as effective antibacterial agents that can be added to bone cement.[1]

Boron is an element used in various fields, ranging from the glass and ceramics industry to construction, cleaning, and medicine. Approximately 40 years ago, boron was thought to have no significant impact on the human body. However, recent studies have demonstrated its positive effects on many systems, particularly in recent years. It has been proposed that boron may play a significant role in osteogenesis, and its deficiency can adversely affect bone development and regeneration.[2,3] Boron has positive effects on wound healing.[4] It also assists in regulating estrogen and testosterone metabolism.[5,6] It has been demonstrated in numerous studies that boron increases vitamin D levels and enhances magnesium

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absorption.[7,8] Due to its anti-inflammatory effect, boron has been used in osteoarthritis patients, and double-blind human studies have shown that the use of boron reduces symptoms to a greater extent compared to the placebo group.[9] In an experimental study assessing the fracture healing effect of hexagonal boron nitride (HBN), it has been mentioned that it can serve as a therapeutic agent to enhance recovery.[10]

In another study, the effects of boric acid, epidermal growth factor (EGF) and their combination on cartilage damage were evaluated and it was mentioned that low dose boric acid could have a positive effect on cartilage healing.[11] There are studies evaluating the effects of boric acid on cartilage lesions, showing that it may benefit cartilage healing.[12,13]

In the present study, we aimed to investigate the effects of adding HBN at four different concentrations to PMMA bone cement, which is commonly used in orthopedic surgeries, on the mechanical properties and microarchitecture of the bone cement.

MATERIALS AND METHODS

In the current study, standard antibiotic-free radiopaque bone cement from Biomet® (Biomet Orthopaedics Switzerland GmbH, Dietikon, Switzerland) in a 40-g quantity was utilized. The HBN in powdered form was sourced from the National Boron Research Institute. A precision scale, Kern PCB 3500-2 from Schramberg, Germany, was employed to measure the cement and boron material weights. Before taking measurements, the containers were tared to zero on the scale. The samples were prepared in the operating room environment at 20±2°C, including an unaltered control group and four different concentrations (40 g of bone cement with 0.5 g, 1 g, 1.5 g, 2 g) of HBN.

Sample preparations and mechanical strength test planning were carried out in accordance with the International Organization for Standardization (ISO) 5833 criteria. To conduct mechanical bending strength tests, samples were prepared in the form of rectangular prisms with dimensions of 75×10×3.3 mm. For compression tests, molds in cylindrical shape with a diameter of 6 mm and a length of 12 mm were prepared (Figure 1). The NC-Z CNC machines were used to create these standard molds and computer systems were employed to minimize the margin of error during mold cutting to the lowest possible level. Steel and plastic casting molds were commissioned to enable the simultaneous preparation of eight samples for bending tests and five samples for compression tests.

The samples were prepared using a manual mixing method. First, 40 g of cement powder and the specified amounts of HBN powders were mixed in a container to homogenize them before adding the liquid component of the cement. Subsequently, the liquid component of the cement was added to this mixture, and the cement was mixed for 2 min. Starting from the second minute, the prepared samples were poured into molds and left to set. The prepared samples were macroscopically evaluated, and any samples that did not have a smooth surface and could potentially yield incorrect results were excluded from the study.

Standard samples with smooth surfaces were selected for the compression test, with eight samples in each group. Likewise, for the four-point bending test, there were 10 samples in each group. These samples were left to set and harden at approximately 23°C for about 24 h in accordance with the standards. At the end of the 24 h, the samples were ready for mechanical testing.

To measure the mechanical durability of the samples, an Instron® 3369 device system (Instron Mechanical Testing Systems, MA, USA) was used for both compression and four-point

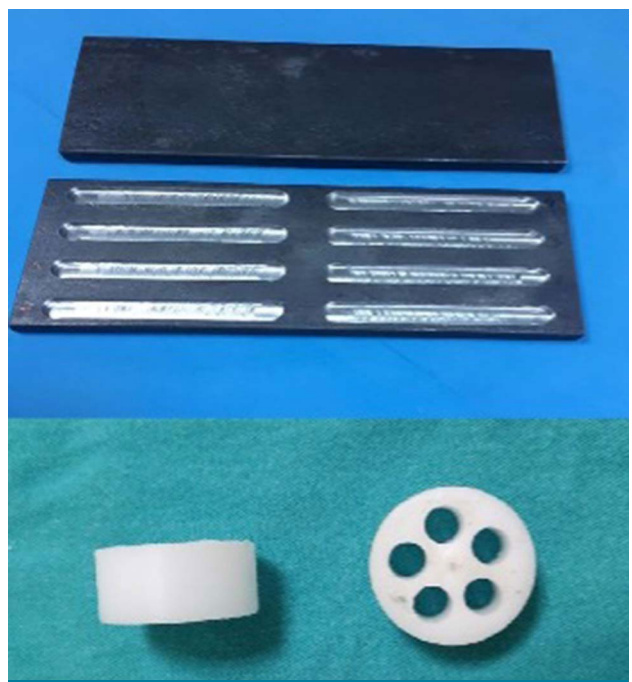


FIGURE 1. Mold types utilized for sample preparation.



FIGURE 2. Four-point bending load test machine. A cement block (arrow) was sandwiched between the for fixtures. The speed of the device was set to 5 mm/min. The maximum four-point bending load was automatically measured when the cement block was fractured.

bending tests, applying forces up to 50 kN. During the bending tests on the samples, precise length measurements were taken between the support points using a length gauge. In accordance with the standards, the distances between the support points at the bottom were set at 60 mm, and at the top, they were set at 20 mm. Precise length gauges were used to mark the midpoint of the samples to ensure proper positioning for the four-point bending test (Figure 2). The speed of the device was adjusted to 5 mm per minute according to ISO 5833:2002 standards. The maximum megapascal (MPa) values that the samples could withstand were determined based on the values at which they broke.

Compression tests were conducted using the same model of equipment, with a compression speed set at 25 mm per minute according to the standards (Figure 3). As a result of the tests, the pressure values at which the samples deformed were determined from the load-deformation graphs, and the MPa values at which the samples exhibited strength were calculated.

For the examination and comparison of the surfaces of randomly selected 1/8 sections of the control sample and samples with varying boron content, a digital and computer-controlled electron microscope, Jeol JSM-6060 LV (JEOL USA, Inc., Peabody, MA, USA), was utilized.

Statistical analysis

Statistical analysis was performed using the IBM SPSS for Windows version 22.0 software

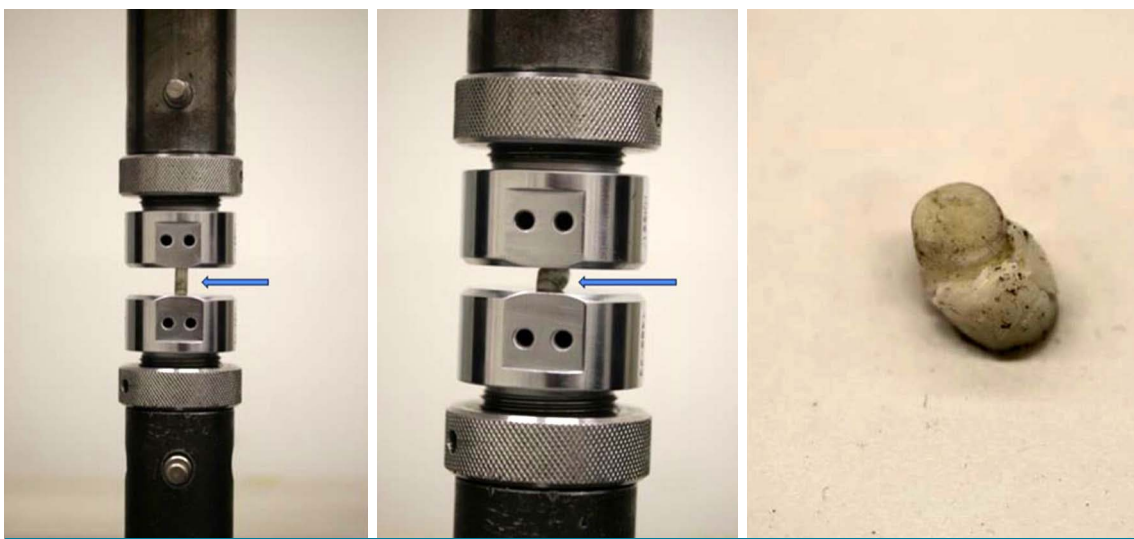


FIGURE 3. Compressive load test machine. A cement block (arrow) was secured between the two arms of the machine, which compressed the cement block at a rate of 25 mm/min. The maximum compressive load was automatically measured when the cement block was crushed.

(IBM Corp., Armonk, NY, USA). Descriptive data were expressed in mean ± standard deviation (SD), median and interquartile range (IQR) or number and frequency, where applicable. The normality of continuous variables was assessed through visual methods (histograms and probability plots) and analytical techniques (Kolmogorov-Smirnov/ Shapiro-Wilk tests). The normality analyses indicated that the data for continuous variables were not normally distributed. To compare between the five groups, the Kruskal-Wallis test was used. The significance of differences in measured continuous variables between pairs of groups was examined using the Mann-Whitney U test. The Spearman correlation test was used to identify the relationship between boron concentration and MPa measurements. A p value of <0.05 was considered statistically significant.

RESULTS

Compression tests

In the current study, the comparison was made between the findings of MPa values from the compression test results of the control group and four different concentration boron groups, comprising 0.5 g, 1 g, 1.5 g, and 2 g of HBN added to 40 g of PMMA. The compression test results for the group with 0.5 g of HBN exhibited statistically significantly higher values compared to both the control group and the samples with higher HBN additions. The mean MPa value for Group 0.5 was calculated at 103.9±1.6, while the control group had a value of 90.5±6.4 (p=0.002). Comparative analysis against the control group demonstrated a statistically significant difference in MPa values for Group 1.5; however, there was no statistically significant decrease in the values

TABLE I
Comparative MPa values in compression testing among groups with varied boron doses

	Mean±SD	Median	Min-Max	*p*
Control	90.5±6.4	90.4	80.8-103.3	***GC vs. G0.5: 0.002*** GC *vs.* G1: 0.093
Group 0.5-0.5 g	103.9±1.6	103.8	101.2-105.6	***GC vs. G1.5: 0.021*** GC *vs.* G2: 1
Group 1-1 g	91.3±14.1	95	57.2-100.9	GC *vs.* G2: 1
Group 1.5-1.5 g	96.1±3.9	95.2	91.9-102.3	***G0.5 vs. G1: 0.001***
Group 2-2 g	89.9±4.5	89.4	83.2-95.9	***G0.5 vs. G1.5: 0.001*** ***G0.5 vs. G2: 0.001***
Boron (total)	95.3±9.2	95.5	57.2-105.6	G1 *vs.* G1.5: 0.753 G1 *vs.* G2: 0.115 G1.5 *vs.* G2: 0.021

MPa: Maximum megapascal; SD: Standard deviation.

TABLE II
MPa values in four-point bending tests across groups with different boron doses

	Mean±SD	Median	Min-Max	*p*
Control	50.6±4.6	50.4	41.1-58.7	GC *vs.* G0.5: 0.821 GC *vs.* G1: 0.070
Group 0.5-0.5 g	50.7±5.1	52.1	41.5-58.8	**GC *vs.* G1.5: 0.034**
Group 1-1 g	55.1±5.2	55.3	47.7-63.3	GC *vs.* G2: 0.326
Group 1.5-1.5 g	54.7±3.9	54.4	50.6-63.4	G0.5 *vs.* G1: 0.070
Group 2-2 g	48.5±3.9	47.6	43.3-53.3	G0.5 *vs.* G1.5: 0.086 G0.5 *vs.* G2: 0.364
BORON (total)	52.2±5.2	52.8	41.5-63.4	G1 *vs.* G1.5: 0.744 **G1 *vs.* G2: 0.007** **G1.5 *vs.* G2: 0.009**

MPa: Maximum megapascal; SD: Standard deviation.

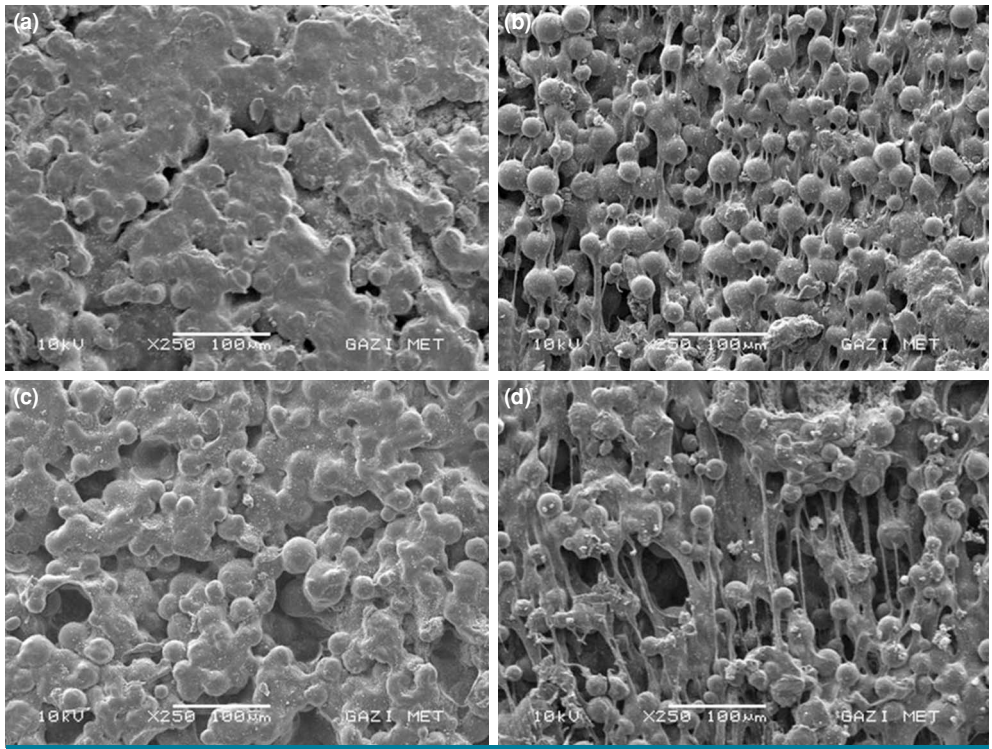


FIGURE 4. The electron microscope image shows cement with boron groups at ×250 magnification, **(a)** depicting Control, **(b)** 1 g, **(c)** 1.5 g, and **(d)** 2 g.

for any other concentration (Table I). However, there was a significant negative strong correlation between boron concentration and compression test MPa values throughout the HBN group ($r = -0.724$; $p<0.001$). This situation was attribute to the difference in MPa between Group 0.5 and Group 2.

Bending strength tests

Comparing the MPa values obtained from the four-point bending test results of the control group and the four distinct concentration boron groups, with the exception of Group 2, all groups exhibited MPa values exceeding those of the control group (50.6±4.6). However, a statistically significant difference was only detected in MPa values between Group 1.5 (54.7±3.9) and the control group ($p=0.034$). Furthermore, statistically significant disparities were noted between Group 2 (48.5±3.9) and both Group 1 and Group 1.5 (Table II). The negative correlation observed in the compression test did not manifest in the MPa values of the four-point bending test ($r = -0.151$; $p=0.357$).

Electron microscope analysis

While examining the electron microscopy images, the addition of 0.5 g of HBN to the cement did not result in a significant increase in porosity compared to the control group. The electron microscopic images of these two groups were quite similar. A minimal increase in porosity was observed in the groups with 1 g and 1.5 g of added HBN. However, a noticeable increase in porosity was evident in the group with 2 g of added HBN. This finding correlated with the mechanical test results, particularly the lower compression and four-point bending test results of the samples in the group with 2 g of HBN added (Figure 4).

DISCUSSION

The results of the present study indicate that the incorporation of HBN at levels below 2 g into the bone cement does not significantly deteriorate the mechanical characteristics of the cement. Indeed, in specific proportions, it yielded substantially higher values compared to the control group. However, mechanical strength and micro-porosity were impacted, when the quantity reached 2 g.

Bone cements, which have been widely used in knee and hip arthroplasty surgeries since the mid-20th century, are considered an evolving subject in parallel with advancements in application

techniques and developments in nanotechnology. Various additives have been incorporated into bone cement in the literature to enhance mechanical strength and improve antimicrobial properties. Particularly in the last three decades, additives have been developed to address these shortcomings.[14] Vitamin E is one of the additives incorporated into bone cement. During the polymerization process, reactions lead to the formation of benzoate and free amine radicals. Vitamin E acts as a scavenger of free radicals. Mixing vitamin E with bone cement has increased cellular compatibility and reduced exothermic activity (from 76°C to 53°C). Furthermore, the addition of vitamin E has been observed to prolong the setting time (from an average of 12.2 min to 20.7 min) without causing a significant alteration in biomechanical properties, as demonstrated in compression and tensile test results.[15] The influence of HBN on the mechanical strength of bone cement, despite its documented positive effects on bone healing and osteointegration,[16] remains an area that has not been extensively explored. Besides, HBN was reported as a promising coating material due to its low density, high thermal conductivity, chemical stability, and easy-to-process structure.[17]

Among other chemicals that can be added to bone cement are barium sulfate and zirconium oxide, which are used to ensure the visibility of bone cement during X-ray imaging.[18] In bone cement with a 10% concentration of barium sulfate, the compressive strength was measured at 85±5 MPa during the compression loading test. However, it was demonstrated that increased concentrations (20%, 30%, and 40%) decreased the compressive strength and four-point bending strength.[19] In the current study, similar to the mechanical results mentioned for barium sulfate, bone cement containing a low amount of boron (0.5 g) yielded higher results in compression tests.[20] As the amount of boron increased, although the strength was higher compared to the control group, compression occurred at progressively decreasing MPa values.

A study examined the variation in corrosion resistance between a control group and PMMA/HBN coated materials with differing proportions of HBN. The findings from the study indicated that materials treated with increasing amounts of HBN demonstrated enhanced corrosion resistance and improved adhesion to the metallic substrate.[21] As the concentrations of HBN increased, porosity and fluidity also increased, suggesting the potential for enhanced compatibility and adhesion of the coating material. Rau et al.[22] evaluated the mechanical and biological outcomes of adding 1% boron nitride to tricalcium phosphate cement by weight. The compression test results demonstrated that the boron nitride group exhibited higher durability than the control group, and no negative effects were observed on osteoblast cell culture. Similarly, in the current study, bone cements loaded with 0.5 g of HBN exhibited increased durability in compression tests. However, in compression tests performed with higher concentrations of HBN, durability did not increase, and a decrease was observed in the 2-g group. The mentioned situation could be attributed to the increasing amounts of HBN leading to increased porosity.

Nonetheless, there are some limitations to this study. First, it is worth noting that the manual mixing method was utilized, and certain test types, such as tensile and shear tests, could not be executed. Furthermore, the temperature of polymerization was not measured. It could be postulated that the manual mixing process may potentially lead to reduced homogenization as opposed to vacuum mixing. To mitigate this potential issue, a preliminary mixing of the cement components with the powdered boron material in a container for 1 min was conducted, followed by a 2-min mixing process at the same speed to render the cement suitable for molding.

In conclusion, the current study demonstrates that adding HBN to bone cement at a low concentration (0.5 g / 40 g PMMA) significantly increases the mechanical strength in terms of MPa (compression forces) without adversely affecting porosity. However, incorporation of HBN at higher concentrations increases porosity, thereby compromising the biomechanical properties of the bone cement, as evidenced by the negative impact on compression and four-point bending tests. Boron-based products have gained increased utilization in the medical field, and HBN is emerging as a promising chemical compound, steadily growing in significance.

Ethics Committee Approval: N/A. The study was conducted in accordance with the principles of the Declaration of Helsinki.

Data Sharing Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contributions: Design: A.P., A.Y., M.A.T., S.Y., A.C.B., H.Y.S.; Analysis and interpretation of data: A.Y., M.A.T., S.Y., A.C.B.; Literature review: A.P., A.Y., H.Y.S.; Writing the article: A.P., A.Y.; Critical review: A.P., A.C.B., H.Y.S.

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