Wear resistance of Polymethyl Methacrylate (PMMA) with the Addition of Bone Ash, Hydroxylapatite and Keratin

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Abstract: In this study mechanical and tribological properties of keratin, bone ash and hydroxylapatite by adding to PMMA (known as the main prosthesis material) were investigated. Hydroxylapatite, bone ash, and keratin materials were added as PMMA in to the content of PMMA, in the proportions of %1, %3 and %5, respectively. The resulting mixtures were put into the molds and solidified in order to obtain samples to be used in the wear experiments. Each experiment was conducted by preparing three experimental samples. The wear data were compared according to the average values of the experimental samples. In the wear test, the results were also evaluated according to the average values obtained from each group and the results of the control group. It was observed that, the wear resistance of the PMMA including 3%, 5% bone ash and PMMA including 5% keratin flour were higher than the values of the control group.

Keywords: Polymethyl Methacrylate (PMMA), Bone Ash, Hydroxylapatite, Keratin, Wear Resistance

1. Introduction

PMMA is an inevitable material because of its characteristics such as its widespread range of mechanical traits, impact maintenance, transparency, optical traits, and compliance with food regulations, bright colors, and its low aqueous absorption. Polymethyl methacrylate (PMMA), which is still in use in commercial bone cement formulations, is a shapeless polymer, polymerized on its own. In the commercially marketed Polybutylmethylemethacrylate PBMA particles are implanted instead of PMMA-styrene copolymer particles. The relative proportions of the other added materials do not exhibit any changes. PMMA has various applications in industry and medicine. PMMA, which has been used in airplane glasses, spectacle lenses, lenses, magnifiers, flasher lamps of the automobiles, bathtubs, production of tubes and manufacturing of various ornaments in industry, has been used with biocompatible bone cement mixtures in medicine. In medicine, PMMA is added to the internal bone fractures with a local reaction. Moreover, it has been used as the base material of prosthesis in dentistry. Many studies have been conducted to improve the maintenance characteristics of PMMA, which has such a wide range of uses. Kinzl et al. (2011) pointed out the effect of PMMA in increasing the porous structure, while they were investigating the mechanical characteristics on PMMA-bone biopsies [1]. Jeremy et al. (1995) identified SRC-PMMA mixture as a composite material and they showed that higher molecular orientation is attained with the thermodynamic pull...
applied on the composite. While the fracture maintenance was measured as 170MPa and tension fault as 5% in the studied fibers with 40 m diameter, the fracture maintenance was found to be as 100MPa and the tension faults as 15% in the fibers with 120 m diameters [2]. Weam et al. (1999) investigated the effect of PMMA powder, which is the essential ingredient of PMMA based bone cement, the conditions related to its different characteristics, its size and molecular weight on the methods of processing, mechanical characteristics and permeability of the bone. By adding different bioactive cements, they showed that while the compression maintenance, elasticity module, the mechanical characteristics such as fracture, hardness improved significantly, bending force very slightly decreased and pulling force significantly decreased [3]. In a study conducted by B. Pascual et al. (1998), modified HPMA cement with a low T/S proportion as 1,86 was used. In order to comprehensively understand the effect of lower T/S proportion, studies were conducted on the exothermic characteristics of polymerization: the mechanical characteristics were tested by means of compression and fracture tests. Polymerization pull and porosity were calculated from the density measurements [4]. In a study conducted by Rodford (1990), polybutadienestyrene copolymers (Macromere) with low molecular weight were used in order to strengthen polymethyl methacrylate. Moreover, butadiene styrene block copolymer with 30% styrene was polymerized by mixing it with methyl methacrylate monomer. The impact maintenance and elasticity module values of the obtained copolymer structures were compared [5].

As can be seen in the relevant studies in the literature, it has been known that the mechanical, chemical and thermal characteristics of the obtained copolymer structure can be improved by means of mixing the copolymers with different characteristics in various proportions, and that this improvement is related to the synergist behaviors of the used polymers [6]. In the present study, by means of mixing bio-cement materials in different proportions, we aimed to make PMMA structure more durable and to decrease the amount of contraction seen in the drying process in the base materials [7].

PMMA has the 18-20 Knoop hardness score and it is relatively hard. It is its contraction resistance is 60 MPa, density is 1,19 gr/cm3 and elasticity module is 2400 MPa [8]. As the organic structures such as keratin, bone ash and hydroxylapatite added within it improves improve the characteristics of PMMA, it is thought that it is use in medicine and dentistry has become more convenient. Keratin is a structurally strong material, which is the base material of nail and horn, insoluble in aqueous. Bone ash has been used in implant treatment in people with bone loss in their mouths, as bone ash is a very similar tissue to the living tissue. As hydroxylapatite present in dentin and bone without getting in the interaction with oxygen, it is expected to exhibit high compatibility. As a result, it is thought that the produced composites might constitute facilitations especially in the field of medicine.

It is aimed to compare the abrasion resistance of acrylic materials by examining the probable erosions of the teeth due to the influence of the jaws moving relative to each other in the mouth.

2. Material and Method

2.1 Bone ash

The bone ash required in the present study was obtained from the grinding of the cow foot bones as a whole. The big particles in the obtained bone ash were separated by means of a sieve, and later they were dehumidified by means of storing them in a dry environment.

2.2 Hydroxylapatite

Hydroxylapatite was produced in the laboratory environment by using reaction method. It is stored in powder form.

2.3 Keratin

Keratin, obtained in liquid form, was stored in 10 ml ampule bottles.
2.4 The preparation of the Mixtures

By means of analytical balance, Bone ash, hydroxyapatite and keratin, 1%, 3% and 5% in weight respectively, were mixed with PMMA, which will be placed in the molds of the experimental samples. Through these preparations, bone ash and hydroxyapatite both in powder form were mixed with PMMA, which was also in powder form, and the final process of the preparations was conducted by means of adding MMA in liquid form to the PMMA mixture. And then the mixture was stored in the molds [9].

Table 1. Hardness values of samples

| Group No: | Group Name:     | Brinell Hardness (Br5) |
|-----------|-----------------|------------------------|
| 1         | Kontrol Grubu   | 20.6                   |
| 2         | %1Bone Ash      | 21.38                  |
| 3         | %3 Bone Ash     | 21.55                  |
| 4         | %5Kemik Tozu    | 22.29                  |
| 5         | %1 Keratin      | 19.16                  |
| 6         | %3 Keratin      | 17.71                  |
| 7         | %5 Keratin      | 13.50                  |
| 8         | %1 Hidroksiapatit | 13.26              |
| 9         | %3 Hidroksiapatit | 17.17             |
| 10        | %5 Hidroksiapatit | 20.27               |

2.5 Preparation of the Test Samples

The metal molds were prepared for the compression test in 16 mm diameter and 18 mm height according to ASTM D695-02a standards, for the charpy impact test in dimensions of 55*10*10 square prisms according to TS EN ISO 179-1 standards and for the hardness tests circular cross section prisms in 16 mm diameter and 16 mm height. The modeling wax poured into these molds in melted form. After the wax solidified, the obtained models were extracted from the molds. For obtaining acrylic resin polymerized with conventional heat, 250 g plaster powder for 100 ml water was mixed and then the resulting mixture was poured the lower part of the muffle. The wax samples were placed into the lower part of the muffle before the plaster was solidified. After the plaster is solidified, varnish was applied. After placing the upper lid of the muffle, plaster was poured. The muffle was placed into the compression with 150 kg/cm² pressure. The plaster was left to solidify for a 30-minute period. In the end of this period, the muffle was opened and the wax models were carefully extracted from the plaster by means of model separator. Isolator was applied to the muffles [2, 10].

2.6 Test Methods

2.6.1 Compression Test. The experimental samples of PMMA-hydroxyapatite, PMMA-bone ash and PMMA-Keratin preparations mixed in 1%, 3% and 5%, respectively, were placed on the compression surface in the given order. After the dimensions of the experimental samples were installed to the
compression device, the experiment was initiated by determining the process speed as 2mm/min. The evaluations were made with reference to the peak points at which cracks were appeared on the surface area of the experimental samples.

2.6.2 Charpy Impact Test. The experimental samples in dimensions of 10*10*55 prepared according to TS EN ISO 179-1 standards were placed on the charpy experimental module. The values after the fractures were recorded in Joule unit.

2.6.3 Hardness Test. The hardness conditions of the samples were found by measuring the resulting trace diameters on the Brinell hardness module by using bits with 10mm diameter under 250 kg load.

2.6.4 Wear Tests. The experiments made are based on the unit obtained by applying abrasive discs 3 and 6, which rotate at 337 rpm, at two different loads of 47 N and 87 N, respectively, to the charging power. Initial weights of the test specimens were measured by means of precision scales and comparisons were made by calculating the evaluation result differences as a percentage. For the abrasion test, the test specimens were prepared with the appropriate dimensions of D: 12.7mm, L: 12.7mm. ASLE (American Society of Lubrication Engineers) has specified from 100 test systems as abrasion tests and measurement methods, the most commonly used abrasion amount, thickness difference and trace change methods. The "weight difference method", which is the most widely used method, is preferred in our experiments.

![Wear test bench and test configuration](image)

**Figure 1.** Wear test bench and test configuration

Measurement of wear loss 1/1000 gr precision scales. Wear can be expressed in general (gr / km), (mg / m) and expressed as weight loss (g / cm2) for the unit area. The following formula is used for the specific erosion of the material. Before the test, the surface of the test samples was polished with sandpaper No. 6 in appropriate dimensions and then the friction surface to do smoothly. The polished samples were weighed before the experiment on the sensitive scale and the initial weight was recorded. The test sample was placed in the test setup and the load, temperature and time values to be the test are determined during apply. The operation is performed by running the test setup [11, 12].

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W_s = \frac{\Delta V}{F_s L} = \frac{\Delta m}{\rho F_s L} \quad [4]
\]

\(W_s\): Amount of specific wear of the material

\(\Delta V\): Volumetric material loss
Δm: Weight loss
P: Density
F_n: Normal force applied
L: Total distance travelled

3. Results and Discussions
3.1 Wear Properties

The results obtained from the wear tests conducted in this study are given below for all samples. It can be seen from the figures that samples behave different according to applied load and sliding duration.

![Figure 2.a.](image1)

**Figure 2.a.** The weight loss of the samples under load of 47N and 3mins.

![Figure 2.b.](image2)

**Figure 2.b.** The weight loss of the samples under load of 47N and 6mins.

The wear test results are given in Fig.2 and Fig.3 under 47N and 87N respectively. It can be seen from the figures that the weight loss results have similar tendency except %3 Hidroksiapatit. When the comparison of the relation between compression and wear
result it can be seen that, although %3 Hydroksiapatit group has the lowest hardness values, their wear resistance are the highest among the others. It can be derived from here that the wear performances of the hard samples are reduced by the microstructures after samples. On the other hand, the homogeneity and porous of the powdered samples have an important role on the wear performance of the material. Hard materials wear perform could be bad affected.

**Figure 3.a.** The weight loss of the samples under load of 87N and 3mins

**Figure 3.b.** The weight loss of the samples under load of 87N and 6mins

On the other hand when the load increased to 87N. Wear resistance values also changed. When the hardness values of the samples are examined, it can be seen that %5 Bone Ash and %5 Hydroksiapatit have best wear resistance values.

All experimental samples were applied the same experimental compression test under the same conditions, same force and same speed and in the conclusion of the experiments.
Table 2. Compression Test Results

| Mixture          | Compression (N) | Charpy Impact (J) | Brinell Hardness (HB) |
|------------------|-----------------|-------------------|-----------------------|
| Kontrol (PMMA)   | 27891.90        | 3.33              | 20.6                  |
| %1 Hidroksiapatit| 23359.15        | 2.63              | 13.26                 |
| %3 Hidroksiapatit| 16473.95        | 2.57              | 17.17                 |
| %5 Hidroksiapatit| 18998.20        | 2.47              | 20.27                 |
| %1 Bone Ash      | 23315.45        | 2.47              | 21.38                 |
| %3 Bone Ash      | 29911.80        | 2.90              | 21.55                 |
| %5 Bone Ash      | 26234.40        | 3.13              | 22.29                 |
| %1 Keratin      | 24446.60        | 2.40              | 19.16                 |
| %3 Keratin      | 21679.90        | 2.67              | 17.71                 |
| %5 Keratin      | 19973.90        | 2.67              | 13.5                  |

In this study we found similar values under 87N. Specially %5 Keratin added group flourished. This group had high wear resistance in addition to toughness according to Table 1. It could be shown us this PMMA could be use with keratin.

It is so important like as toughness wear resistance values specially in dental industry. Otherwise this group of compression resistance can improve. In dental using PMMA which is dental implant material always expose compression forces.

One of the biggest advantage %5 Keratin PMMA group it is the cheap material.

4. Conclusion

The conclusions derived from this study can be follow as

1. In the 18-20 age group, the average of the bite force is 176N. If considered to be, the 87N group was examined as the closest value, and in these groups, the mass loss of the 5% keratin group decreased significantly compared to the control group.
2. Variable findings were found as a result of the abrasion tests conducted and it was observed that the 5% keratin-PMMA and hydroxyapatite-PMMA groups had higher wear resistance under high loadings as a general wear resistance and especially the 5% keratin-PMMA mixture gave better results than the control group.
3. Considering an acrylic exposed to continuous wear in the mouth, it was observed that the 5% hydroxyapatite group could give better results.
4. It was seen that the sample with 3% bone ash mixture yielded better results in comparison to the control group.
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