Hardness evaluation of PMMA reinforced with two different calcinations temperatures of ZrO$_2$-Al$_2$O$_3$-SiO$_2$ filler system

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Abstract. Polymethyl methacrylate (PMMA) is one of the materials used for the temporary crown while making fixed partial dentures. Unfortunately, it has low mechanical properties. This study aims to improve PMMA hardness by adding ZrO$_2$-Al$_2$O$_3$-SiO$_2$ filler system in two different calcination temperatures. Thirty-two disc form samples with 8mm diameter x 3mm thickness were made from two category-filler based that had been previously evaluated using Scanning Electron Microscope (SEM). Each category was divided into six groups of three respectively from a controlled and different concentrations of 7(A), 9(B), 11(C), 13(D), and 15(E) weight % of reinforced filler system, then tested with Vickers Hardness Tester. Filler particles that calcined at 550° can increase to 700° consist of fine crystalline and amorphous phases; however, the sample shows the highest hardness about 20.19 VHN even though the increase is only 7.5% compared to control. Meanwhile, the sample that calcined at 700°C exhibits the highest hardness about 15.66 VHN corresponds to sample D. it has increased 25% compared to the control. This is correlated with microstructure result that has more growth crystalline particles. The results were analyzed by ANOVA which determined were not statistically significantly different (p<0.05). Therefore, it can be concluded that the 13% reinforced ZrO$_2$-Al$_2$O$_3$-SiO$_2$ filler system calcined at 700°C shows the highest hardness increase compared to calcination temperature 550-700°C. Although it is not significantly different.

1. Introduction
Dental aesthetic plays a very important role in life since most of the people want their teeth to look natural. Even Skinner, in 1959 has already noted that the aesthetic quality of the restoration is important to dental health as well as the mental health of the patient. Nowadays, aesthetic consideration are still primary factors for seeking various dental treatments, especially in indirect restoration as their steadily grows to restore the dentition naturally [1], [2]. Implant supported ceramic restoration is one of the treatments chosen for partially and fully edentulous patients since this fixed prosthesis type almost similar to the natural dentition. Besides, its success rate has been shown to be over 90% [2].

Implant fixed prosthesis could be made with two steps approach, which is firstly the surgery that takes several months to wait for the osseointegration process and healing phase of the soft tissues surroundings. Those conditions are very important in implant treatments as their successful outcomes, which are crucial due to the high costs of ceramic dental implants. Usually, the conventional protocols should take 3 to 6 months to allow the osseointegration process to take place [2], [3]. Secondly, the
fabrication of crown or fixed partial denture (bridge) is a laboratory-based procedure, which needs time-consuming procedures, highly trained technician, and several weeks or some months may lapse between the preparation of the teeth and the cementation of the permanent restoration [4], [5], [6]. Since the treatment could take several months for final restoration, thus a temporary restoration be provided. This temporary restoration then needs to be strong, durable and aesthetic to last throughout the duration of the treatment [2], [7].

Acrylic resin or Polymethyl methacrylate (PMMA) is a polymer that is commonly used in dentistry, especially for indirect restorations such as denture base material and provisional crown jackets [8], [9], [10], [11]. This material has been chosen based on its aesthetics, fabrication method, and economic point of view. However, its low mechanical properties limited the clinical use of restorative materials [10], [11], [12].

Several attempts have been done to increase the mechanical properties, such as the addition of structural component including metal and ceramic, by adding filler particles with different elements such as zirconia, silica, alumina, glass fiber, tin and copper to PMMA [12], [13], [14], [15], [16], [17]. The incorporation of inorganic nanoparticles into PMMA alters the properties of the end product depending on the type, sizes, and shapes, concentration, and interaction within the polymer matrix itself [16].

In presuming a long term use of the provisional crown, in 2015, a study has been done to increase the mechanical properties of PMMA by the reinforcement with self-synthesized of $\text{ZrO}_2 - \text{Al}_2 \text{O}_3 - \text{SiO}_2$ filler system using sol–gel technique and coating with two types of silane coupling agent. It was found that type and percentage of coupling agent affected the PMMA filled [18].

Based on the research data above, the effect of different temperature treatment to the fillers have not been studied yet. This study aimed to continue the work which is comparing the hardness of PMMA reinforced with $\text{ZrO}_2 - \text{Al}_2 \text{O}_3 - \text{SiO}_2$ filler system that synthesized and calcined at two different calcination temperatures (at $550^\circ\text{C}$ for 1 hour and increased to $700^\circ\text{C}$ while the other directly heated to $700^\circ\text{C}$) using different ratios of PMMA powder: The variations ratio of PMMA to filler system are 7, 9, 11, 13 and 15 wt%.

2. Materials and Methods

The research procedures were divided into 3 stages consists of the preparation of ceramic particles of $\text{SiO}_2 - \text{Al}_2 \text{O}_3 - \text{ZrO}_2$, provided PMMA samples filled with the ceramic particles, and then tested with the hardness test.

2.1. Preparation of Ceramic Particles

a. Synthesis of ceramic nanoparticles. Ceramic nanoparticles composed of zirconia-alumina-silica were prepared using sol-gel techniques as mentioned by Hasratiningsih et al (2015). Aluminum nitrate nonahydrate, tetraethyl orthosilicate, and zirconium chloride were used as precursors for alumina, silica, and zirconia, respectively. Distilled water and 1%w/v chitosan were used as solvent and dispersant, respectively. Briefly, the precursor with the proportion of 10% alumina, 70% silica, and 20% zirconia was employed and mixed homogeneously followed by hydrolysis and condensation process. The prepared ceramic was ultra stirred and homogenized using ultrasonic homogenizer, and also dried at 100°C. Afterward, heat treatment was applied. The ceramic powder obtained were divided into two calcination temperatures. Firstly, the powder was calcined at $550^\circ\text{C}$ for 1 hour then the temperature raised to $700^\circ\text{C}$. Secondly, the other powder was heated directly to $700^\circ\text{C}$ for two hours. Both were heated in an electric furnace (Cress Electric Furnace C1228/935, Carson City, Nevada). The powder obtained then characterized its structure and morphology [18].

b. Filler coating process. The ceramic filler system of Silica - Alumina - Zirconia was silanated with chitosan 1%. The coupling process was developed based on Hasratiningsih work (2015) with minor modification. Briefly, prepared the chitosan 1% solution using 1 gram of chitosan powder, 2 ml of 100% acetic acid and 98 ml aquabadest. Mix the chitosan powder and acetic acid in aquabadest use magnetic
stirrer for ± 30 minutes until all the chitosan has dissolved. Then put both ceramic powders into two beaker glass and soaked in coupling agent followed by centrifugation. Next, the powder was dried in vacuo. The powder obtained was then crushed and stored at room temperature.

2.2. PMMA Sample Preparation
Two categories of samples according to two different calcination temperatures were prepared (each category consists of 18 samples including control). A total of thirty six samples were made using a conventional method as processing acrylic dentures using heat cured acrylic resin (De Trey® Stellon C Rapid Shade 3). Briefly, the wax patterns were made in molds (made of Teflon® PTFE) with a dimension of disc form with 8 mm in diameter and 3 mm in thickness. Gypsum molds were prepared by investing the wax pattern using dental stone in dental flasks then immersed in boiling water. Afterward, the softened wax was taken out and flushed with boiling water added to detergent to remove any impurities and to facilitate the application of separating medium (Cold Mold Seal). The mold cavities obtained were used for the preparation of test samples.

The ratio of PMMA heat cured resin polymer and monomer used was of 1:2 by weight was mixed and packed into the mold and used as a control. The flakes were put in the water at room temperature then raised until boiled within 1 hour. After that, the flakes were kept for 1 hour to continue the polymerization. The samples were deflasked after bench cooling. PMMA added with zirconia-alumina-silica coated by coupling agents were mixed with resin then packed in the mold. The percentage of each filler (two different calcination temperatures) used were 7, 9, 11, 13 and 15% consecutively then cured. Each sample was prepared accordingly. Prior to hardness test, all samples were stored in water bath 37°C for 24 hours.

| Category I Groups | Category II Groups | Description |
|------------------|-------------------|-------------|
| A                | A1                | Unfilled acrylic resin (PMMA) without ZrO₂-Al₂O₃-SiO₂ filler system as control |
| B                | B1                | PMMA with 7% ZrO₂-Al₂O₃-SiO₂ |
| C                | C1                | PMMA with 9% ZrO₂-Al₂O₃-SiO₂ |
| D                | D1                | PMMA with 11% ZrO₂-Al₂O₃-SiO₂ |
| E                | E1                | PMMA with 13% ZrO₂-Al₂O₃-SiO₂ |
| F                | F1                | PMMA with 15% ZrO₂-Al₂O₃-SiO₂ |

2.3. Hardness Test
The novel composites produced were then subjected to the hardness test. The tests were performed onto the surface of each sample by means of Mietkovickers and determined using Vickers hardness tester machine, LECO - Japan M - 400 - H1/H2/H3 with a load of 200 grams for 15 seconds (ADA Specification No. 27). Five indentations were equally placed over the surface of each specimen and not closer than 1 mm to the adjacent indentation. The tests were conducted at the Laboratory of metallurgical physics and ceramics, Faculty of Mining and Petroleum Engineering, Institute of Technology Bandung.

3. Results and Discussion
Temporary crown and bridge materials are mostly made from uncross-linked acrylic polymer. The composition and manipulation are essentially the same as for denture bases. Mostly the acrylic polymers in dental prostheses are homopolymers (one type of monomer unit) that have no crosslinks. Compared
to cross link resin this PMMA has lower mechanical properties [4]. This study aimed to develop PMMA reinforced with better mechanical properties. The samples prepared in this study mostly by manual while some of the procedures are technique sensitive so the samples made according to the categories were prepared in one series (i.e., control & different groups).

Mokhtar et al. 2013 observed the crystallization of tetragonal zirconia start showing up at 500°C and the pattern of this crystallization are more intense upon increasing the calcination temperature according to XRD analysis. The intensity will continue until 700°C, but at the temperature above 700°C, the monoclinic crystalline will start to appear. The filler prepared using calcination temperature at 700°C based on the theory that high mechanical properties associated with the high intensity of the crystallinity of filler particles. The higher the crystallinity of the filler the better the mechanical properties are. The crystal structure and phase formed are also influenced by calcination temperature and heat treatment process that the crystallinity increased with increasing calcination temperature [18], [19].

Zhang and Choy (2015) figured that 100% tetragonal zirconia phase was formed at temperature 700°C in Yttria-Stabilized Zirconia. At temperature 800°C tetragonal phase decreased to 97.1% followed by unexpected monoclinic phase was coming up. This condition was followed by an exothermic peak at temperature ~790°C. The higher the temperature used, the higher amount of monoclinic crystalline was formed. Although in this study was using alumina instead of yttria as a stabilizer, it seems that phenomenon aforementioned was found as well. Besides zirconia, silica was added to compensate the opacity of zirconia and alumina. The additions of the other oxide to zirconia, like silica, not only to improve optical properties but also alumina can act as stabilizing oxides as well, which then given treatment temperatures [17], [18], [20], [21], [22].

Silica has 3 different crystal phases, such as quartz, tridymite, and cristobalite. The silica when is heated, a change in crystalline form occurs at a transition temperature characteristic of the particular form of silica. The best silica crystal phase, according to Ted Pella (2015) is beta - quartz which generates scale 7 on the Mohs hardness. Beta-quartz crystal phase will be formed at a temperature of 573°C - 870°C [9]. At high temperature (550 - 700°C) the peaks and intensity of the zirconium crystal phase suggest that tetragonal phase coexists with the monoclinic and cubic phase [18]. Both are main reasons for calcination temperature that were used in this research consist of two different temperature. A temperature of 550°C for 1 hour then raised to 700°C temperature and the other one that directly raised from room temperature to 700°C then maintained it for 2 hours.

Figure 1 shows the diagram of Vickers hardness number of the samples which calcined at 550°C for 1 hour then raised to 700°C (a) and samples that calcined only at 700°C (b). There was no statistically significant for group 1. Meanwhile, group 2 shows statistically significant between 7%, 9% and 11%.
samples. However, these significances were not revealed when compared to control in each group. These were supported by ANOVA analyzed. In other words, the temperature parameter that was employed in this study has not given any different effect of increasing the Vickers hardness number.

The reason based on this hardness test results are quite related with the prediction of transformation toughening mechanism. The additions of Al₂O₃ can discontinue transformation that shows the volume fraction of stress-induced transformation is definitely not uniform across the zone width. The other prediction is that system of ZrO₂-Al₂O₃ can transform to stacks of monoclinic twins. In both classes of material, the adjacent pairs of twins provided an extremely effective means of accommodating the shear component of the transformation shape strain [20].

Ayad, Badawi and Fatah (2008) found the addition of zirconia treated with zirconate (6% and 15%) increased the transverse strength of acrylic resin but no significant difference was detected for surface hardness. However, Ahmed and Ebrahim (2014) suggested that Zirconium oxide nano-fillers was increased the flexural strength and hardness of the acrylic resins significantly using 7% wt ZrO₂ concentration but did not explain about silanization.

Shirkavand and Moslehifrad (2014) in their study found the various ratio of TiO₂ reinforced PMMA increasing the mechanical properties in certain concentration then decreased by additional more amount of TiO₂. While Asopa et al (2015) studied using zirconia filler found the same phenomena on the strength properties of the PMMA reinforced. On the other hand, the hardness was decreased.

Our result showed support Ahmed and Ibrahim work (2014), but in contrary with Asopa et al (2015). In this study filler used were ZrO₂-Al₂O₃-SiO₂ coated with chitosan 1% as a coupling agent. Coupling agents are used to linking the filler to the polymer. Silanization of the filler surface gives the ability of composite to distribute stress from the matrix to fillers. A silane/coupling agent acts as a sort of intermediary between organic materials to inorganic materials. The hydrogen bonding allows bonding between organic and inorganic material as well as promoting adhesion by forming chemical bonding with resin [9], [21].

Both factors filler system and coupling agent used increased the filler: PMMA ratio and hardness at a certain ratio. The reason as [10] because the additional of fillers (TiO₂ in their study) act as impurities and the strength decreases as a result of the extra additive. Improper dispersion of the filler in PMMA matrix unfavorably affects the reaction of monomers, leading to increased levels of uncured monomer, which acts as a plasticizer. The increased in filler content cause these particles to agglomerate. The agglomerated compounds can act as stress concentrating center in the matrix and adversely affect the mechanical properties of the polymerized material [10].

That statement supported by Asopa et al (2015) that the increase in the filler fraction does not necessarily lead to increase in the strength. However, because excessive filler fraction creates more defects the material weakens. So that percentage of filler used (zirconia) for reinforcement should be such that the filler particles should disperse event into the resin matrix without interrupting the continuity of the resin matrix. The effect of higher filler content on reducing strength can be explained on the basis that after reaching saturation point the resin cannot incorporate furthermore filler particles. Any attempt to add filler particles after reaching saturation of matrix leads to an interruption in the resin matrix continuity and thus causing a decrease in the strength of the reinforced specimens. On the other hand, there finding the addition fillers in any ratio decreased the hardness value compared to control group [12]. In this study, the decrease of hardness was found when the filler added more than 11 wt% of the filler calcined at 550 and 13 wt%.

4. Conclusions
The 13% reinforced ZrO₂-Al₂O₃-SiO₂ filler system at 700°C shows the highest hardness increased about 25% compare to calcination temperature 550 - 700°C. Although it has not statistically significant difference, this reinforcement may improve PMMA mechanical properties.
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Acknowledgment
The authors were grateful to Directorate of Higher Education Ministry of Research, Technology and Higher Education, the Republic of Indonesia through Padjadjaran University for funded the research.