Synthesis of Metakaolin-zirconia-apatite Nanocomposite for the Application of Direct Teeth Restoration

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Abstract

The increased use and research on direct composite restorations materials are mainly attributed to the demand for esthetic and excellent strength restorations. Early composites that were used for restoration process tend to had unfavorable properties, such as weak and having bad interaction with teeth interface. Combination of metakaolin-zirconia-apatite can yield a very good composite for teeth restoration application. It produces high hardness and good interaction with the teeth. The Vickers hardness test showed that metakaolin-zirconia-apatite nanocomposite produce excellent hardness, which reac h 37.5 VHN. The Scanning electron microscope characterization showed that there were no shrinkage observed on the interface of the teeth in the application of the nanocomposite as the restoration materials. From this result, it can be said that the composite has a good interaction with the teeth for the restoration application.

Keywords

Restoration; Teeth; Nanocomposite; Hardness; Shrinkage

Introduction

Dental health is a reflection of the overall human health. The main issues related to the health of the oral cavity until now are still on dental caries and gingivitis. Dental caries is a disease which damages the structures of teeth. Dental caries is characterized by demineralization email minerals and dentin, followed by damage to organic materials (Kidd and Smith, 2000). Perforated or damaged teeth can be treated by restoration process. Based on the method of placement, restoration is divided into two types, which are direct and indirect restoration. Composite is one of the most common used direct restoration materials now days. The reason is because by using composite materials, a lot of properties that are necessary, such as mechanical properties and elasticity properties, can be adjusted and combined to match the real teeth properties (Anusavice, 2003).

Composite resin consists of three main components, namely: organic components (resin) that form the matrix, fillers, and coupling agent. In addition to these three main components, the composite resin also contains the color pigments in order to produce the same composite color as the real teeth and initiator-activator materials to activate the hardening mechanism (Anusavice, 2003).

Along with the development of nanotechnology, recently composite materials has been developed using the nano-sized filler. These composites, which are in nano size, are called nanocomposite. These composites have a smooth surface structure and good mechanical properties (Roberson et al., 2006; Powers and Kaguchi, 2006; Bandyopadhyay, 2008). According to previous research, the nanocomposite can be synthesized from alumina-zirconia-silica (Faza, 2011). Another study states that the nanocomposite material can be synthesized using zirconia-magnesia-calcium for dental restorative materials applications (Putri, 2011). Various modifications continue to be developed in order to obtain better nanocomposite mechanical properties one of which is using a mixture of synthetic inorganic materials such as zirconia, kaolin, and apatite.

Zirconia has been used in dentistry for its strength, hardness and high fracture resistance. Another study states that the alumina (Al_2O_3) can be used as a stabilizer in zirconia (Pratama, 2011). Alumina is an extremely hard ceramic, bioinert, heat resistant and chemicals resistant (Evelyna, 2010). Combination of alumina and zirconia tend to produce restoration material with unfavorable aesthetic properties. It is required to combine the alumina and zirconia with other materials that have good translucency, like silica, to improve the aesthetic value (Ayu, 2010). Both alumina and silica can be found in the kaolin material.

Kaolin is a type of geopolymer material, which is based geopolymer alumia-silica (Al_2O_3 and SiO_2), that can be activated by a strong alkaline solution (Nicholson and Fletcher, 2005). Kaolin is composed of clay material with low iron content. Kaolin has a composition of aluminum silicate hydrate (Al_2O_3 $2SiO_2.2H_2O$). In the ceramic industry, the addition of kaolin serves to improve the quality of the product colors by make it brighter and more powerful. This is because the kaolin contains small amounts of iron and titanium ions. Besides zirconia and kaolin, in this study apatite materials also been added to increase the hardness and the biocompatibility of the composite.

The combination of metakaolin-zirconia-apatite aims to produce resin composites with better mechanical properties. Synthesis of metakaolin-zirconia-apatite can be hardened by self-cure polymerization (chemical method), which is quite inexpensive and the polymerization process itself tend to reduced the potential of shrinkage. The hardness property is essential to determine the viability of the composite inside the oral cavity.

Methodology

Tools

Equipments that were used: magnetic stirrer, digital scales (max 100 g ± 0.001 g), measuring cups, beakers, dental curing light, calcination equipment, pipette, spatula, mylar strip, and mortar.

Material

The materials that were used: ZrCl4, $Ca(NO_3)_2$, $(NH_4)_2PO_4$, CaO, NaOH, ammonia, chitosan, demineralized water, and commercial nanohybrid composite.

Process

Precursor Preparations

1) Geopolymer Binder

Geopolymer binder was produced by firing the kaolin at 850^{o}C for 6 hours. The result of this process was metakaolin that was used as the binder.

2) Zirconia Preparations

Zirconia was prepared using sol-gel method. $ZrCl_4$ 0.1 M, mixed with chitosan 2%, was fired at 900^{o}C to produce the zirconia powder.

3) Apatite Preparations

Apatite was prepared using $Ca(NO_3)_2$, $(NH_4)_2HPO_4$, and ammonia. The result of mixing these three materials was white precipitate, which was the apatite.

Synthesis of Nanocomposite

The prepared precursors, which were the metakaolin, zirconia, and apatite powder, were mixed with three different composition: 3:1:1, 8:1:1, and 10:1:1. Each of this composition then was combined with CaO. This powder mixture then was mixed with liquid phase containing NaOH 14 M, waterglass, and aqua demineralization.

Comparison with Commercial Nanohybrid Composite

The nanocomposite that was produced then was compared with Fusion – light cured universal nanohybrid composite. Both of the composites were used as restoration materials for teeth. The commercial nanohybrid used the light-cured method for the curing process. The comparison consists of the mechanical properties and the interaction of the composite with teeth interface.

Characterization

To know the crystallinity and phase of the Apatite, X-Ray Diffraction (XRD) characterization using Phillips Analytical X-ray BV Based PW 1710 was then used. The hardness level of the nanocomposite was then tested using microvickers hardness tester.

In addition, the Scanning Electron Microscope type JEOL (JSM-35C) was used to determine the morphology of the nanocomposite and its interaction with teeth interface.

Result and Discussion

XRD Characterization

The diffractogram which is shown in Fig. 1 showed the existence of peaks at 2θ 27.72°; 29.58°; 30.98° dan 34.37°. This peaks represent that the apatite that was whitlockite. It fits the peaks that was observed in

Powder Difraction File (PDF # 09-01690:047), which the standard pattern diffraction for whitlockite.

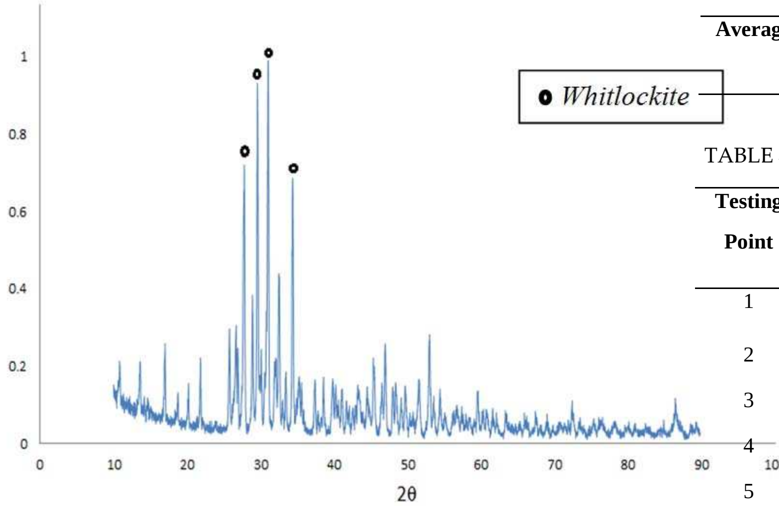

FIG. 1 DIFFRACTOGRAM OF THE APATITE

Vickers Hardness Test

The three nanocomposites that were synthesized with different composition and the commercial nanohybrid composite were then tested with the microvickers hardness tester. The results of each sample can be seen in Table 1, Table 2, and Table 3 below.

TABLE 1 SAMPLE 1 (METAKAOLIN-ZIRCONIA-APATITE=10:1:1)

Testing Point	Day 1 (VHN)	Day 2 (VHN)	Day 3 (VHN)	Day 4 (VHN)	Day 5 (VHN)	Day 6 (VHN)
1	11.40	19.40	23.40	22.30	28.80	21.60
2	11.50	21.40	16.60	22.30	25.80	26.20
3	10.80	18.30	24.50	18.90	23.10	23.40
4	12.00	16.90	26.70	20.00	22.20	20.70
5	09.50	17.10	23.10	20.70	20.60	19.90
Average	**11.04**	**18.62**	**22.86**	**20.84**	**24.10**	**22.36**

TABLE 2 SAMPLE 2 (METAKAOLIN-ZIRCONIA-APATITE=8:1:1)

Testing Point	Day 1 (VHN)	Day 2 (VHN)	Day 3 (VHN)	Day 4 (VHN)	Day 5 (VHN)	Day 6 (VHN)
1	09.20	25.80	29.70	26.70	38.00	23.20
2	11.60	18.00	23.00	35.70	42.50	42.60
3	08.90	24.80	28.10	24.00	34.70	39.60
4	10.20	21.80	32.80	43.50	32.40	37.40
5	10.10	20.60	30.90	29.30	31.00	37.90
Average	**10.00**	**22.20**	**28.90**	**31.84**	**35.72**	**36.14**

TABLE 3 SAMPLE 3 (METAKAOLIN-ZIRCONIA-APATITE=3:1:1)

Testing Point	Day 1 (VHN)	Day 2 (VHN)	Day 3 (VHN)	Day 4 (VHN)	Day 5 (VHN)	Day 6 (VHN)
1	7.70	14.10	39.40	34.60	33.80	37.90
2	6.70	12.00	29.10	32.00	34.20	38.00
3	8.40	11.70	35.10	32.30	41.00	32.20
4	7.20	15.70	29.40	33.90	34.10	37.80
5	6.70	12.90	31.50	29.50	34.90	41.60
Average	**7.34**	**13.28**	**32.90**	**32.46**	**35.60**	**37.50**

From the result, it was observed that nanocomposite with composition of metakaolin-zirconia-apatite=3:1:1 produce the highest hardness, which was 37.50 VHN after six days process of polymerization. The higher composition of zirconia that was used tend to create stronger composite.

The commercial nanohybrid composite that was cured using light-cured method also was tested using the microvickres hardness tester and showed hardness result 27.16 VHN. This hardness level was actually lower compare to the hardness of metakaolin-zirconia-apatite nanocomposite that was synthesized after a few days of polymerization process.

SEM Characterization

The differences in morphology between the nanocomposite that was synthesized and the commercial nanohybrid composite were observed in

Fig. 2. Nanocomposite that was synthesized has a better interaction with teeth when it was applied as restoration material. It is said because there was no shrinkage found at the SEM result on the interface between the composite and the teeth, while the use of commercial nanohybrid composite tend to create shrinkage with size around 2.3 μm-11.1 μm.

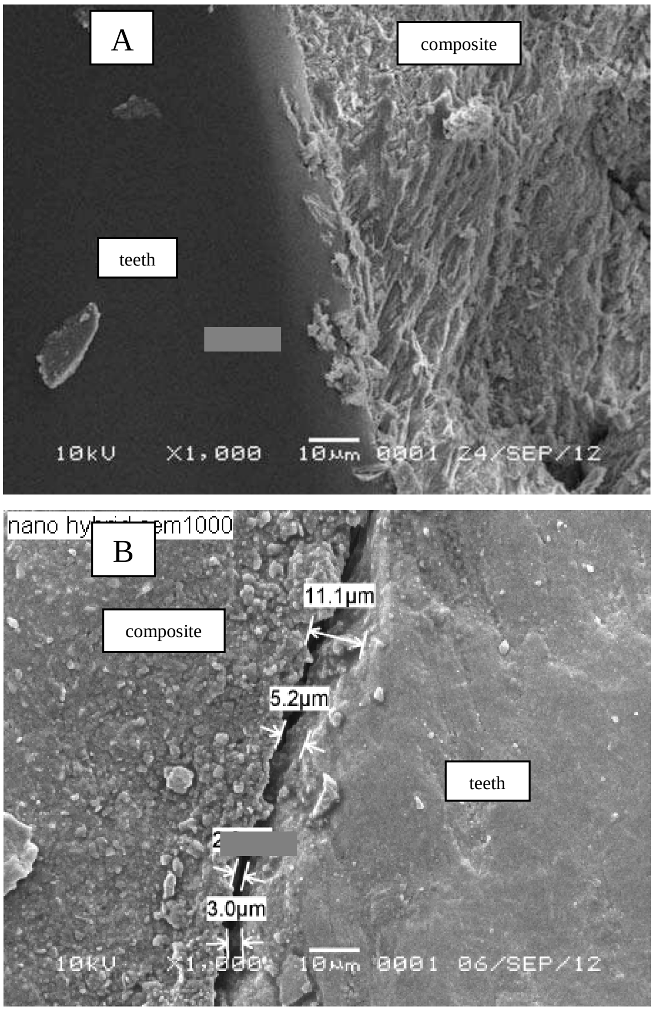

FIG. 2 INTERACTION BETWEEN TEETH AND (A) METAKAOLIN-ZIRCONIA-APATITE NANOCOMPOSITE, (B) COMMERCIAL NANOHYBRID COMPOSITE

Good interaction between the composite and the teeth interface will prevent the potential of failure in teeth restoration process.

Conclusions

Metakaolin-Zirconia-Apatite Nanocomposite have been successfully synthesized with mechanical property exceeding the commercial nanohybrid composite. The nanocomposite with metakaolin-zirconia-apatite composition 3:1:1 produce hardness about 37.5 VHN, higher compare to commercial nanohybrid composite which is 27.16 VHN. The use of metakaolin-zirconia-apatite nanocomposite as restoration material also showed good interaction with the teeth, while commercial nanohybrid composite tend to create shrinkage at the interface that connect the composite and the teeth. This good interaction has potential to prolong the lifetime of the restoration material in oral cavity.

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