ORIGINAL ARTICLE

Dental Cement Preparation of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) with Addition of Filler Aluminum Oxide (Al_2O_3)

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ABSTRACT

Introduction: The quality of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) dental cement could be improved by the addition of Aluminum Oxide (Al_2O_3). It was caused by the characteristic of alumina which are easy on fabrication process, resistant on corrosion, endurance usage, bioinert, and biocompatible. The purpose of this study was to determine the effect of the addition of Al_2O_3 in ZOE-EBA cement. **Methods:** Nanoparticle of ZnO (zinc oxide), Al_2O_3, MgO (magnesium oxide),eugenol liquid and EBA (Ethoxy Benzoic Acid) fluid. The variations of Al_2O_3 were 24%, 26%, 28%, 30%. First is the sintering on 1000°C and tested by XRD. Sintered powder was mixed with liquid, with a ratio of powder: liquid 7:1. The mechanical characteristic are compressive strength and hardness. **Results:** XRD test is showed that ZnO has dominant phase on the sample and there was new phase on cement powder such as Zinc-Aluminium oxide ($ZnAl_2O_4$). The best result was shown on the addition of 26% of Al_2O_3 composition in the 3 type test because the sample had $ZnAl_2O_4$ phase volume fewer than 28% and 30% of Al_2O_3. This result was supported by the compressive strength and hardness which showed the optimum value at concentrations of 26%, which were 64.49 MPa and hardness of 69.33 VHN. **Conclusion:** Based on the result, it was found that Al_2O_3 variation gives the best results in the teeth ZOE-EBA cement was 26%.

Keywords: Dental Cement, Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE- EBA), Variation of Aluminium Oxide (Al_2O_3)

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INTRODUCTION

Dental caries or cavities is a common dental problem. Dental caries is mostly experienced by 90% of Indonesian people (1). Furthermore, from the results of the 2004 Household Health Survey (SKRT) conducted by the Ministry of Health, the prevalence of dental caries in Indonesia is 90.05%. This caries phenomenon causes the need for tooth restoration. One of the biomaterials used for dental restoration is cement (2).

Temporary dental cement must meet several conditions in its use. Some of these conditions include resistance to acidity, high compressive and tensile strength, resistance to plastic deformation, biocompatibility, long-term working time in the mouth, heat insulation. This temporary dental cement must also be bacteriostatic and not easily dissolve in saliva (3).

Zinc oxide eugenol (zinc oxide eugenol) is the most widely used type of dental cement. The use of zinc oxide eugenol cement is inseparable from the many advantages it has, namely, it can reduce pain in the dental pulp, has antiseptic properties, can adapt well to cavity, does not irritate the pulp so that it can be used as a temporary patch (4). This temporary dental cement is expected to be able to make the pulp healthy before a permanent lift is carried out. Besides its advantages, eugenol zinc oxide cement also has weaknesses in its mechanical properties, namely: low compressive strength, hardness and its solubility (5).

Efforts to increase strength in the ZOE dental cement can be done by providing certain material choices. In study by Brauer GM et al, they were added Aluminum Oxide (Al_2O_3) and Ethoxy benzoic acid (EBA) microparticles in to ZOE-EBA dental cement (4). This is due to the easy nature of alumina in the fabrication process, good corrosion resistance, durability long enough use,

bioinert and good biocompatibility. Aluminum oxide is a very effective reinforcing agent for ethoxy benzoic acid(EBA.)cements. Addition of Al_2O_3 increases the amount of powder that can be incorporated into the mix.The compressive strength of the hardened cement is increased up to 1055kg/cm(15,000p i)and the ADA film thickness decreased to 26u. The materials adhere to tooth structure as well as zinc phosphate cements and are suitable as crown and bridge cements.With higher powder-liquid ratios their highten minute compressive strength and excellent tissue tolerance suggests their use as bases under metallic restorations.While the nature of Ethoxy Benzoic Acid (EBA) is to have a low melting point, non-corrosive and not easily dissolved in water. The addition of this mixture is often called ZOE-EBA (Zinc Oxide Eugenol-Ethoxy Benzoic Acid). The result of this addition makes ZOE dental cement have physical properties namely low solubility level and compressive strength which is increasing, but still low when compared with other dental cements (6).

Based on the above background, research is needed to determine the effect of the addition of Aluminum Oxide (Al_2O_3) with the size of nanoparticles to the compressive strength and hardness of ZOE-EBA dental cement. Tests carried out are physical properties tests. The physical properties test include hardness and compressive strength test which are used to determine the sample's resistance to pressure deformation and to determine the ability of the dental cement to withstand the load. Structural properties test using X-Ray Diffraction (XRD) determine the crystal structure formed from ZOE-EBA dental cement.

MATERIALS AND METHODS

Synthesis of samples

The preparation of the ZOE-EBA dental cement sample through several stages. The first stage is the manufacture of cement powder. Test samples were made from zinc oxide with the addition of magnesium oxide made equal to 3% so that the variation of the composition of aluminum oxide was 24%, 26%, 28%, 30%. Weighing the dental cement powder according to the ratio of the composition determined (Table I). Then mix the ZOE-EBA cement powder using High Efficiency Milling (HEM) so that the compounds are mixed homogeneously. The ZOE-EBA cement powder mixture was sintered using Furnace at 1000 °C for 1 hour. The second stage is the process of mixing the powder and cement liquid (a mixture of eugenol and EBA liquids with a composition of 37.5% eugenol and EBA 62.5%). In this study the ratio between powder and liquid is 7: 1.4. This arrangement was to compensate with the alteration in the dentinal surfaces (7). The steps to be used are to prepare powder and liquid weighing 1.4 g and 0.2 ml, respectively. Mix the cement powder and liquid manually until it is homogeneous using a spatula on the glass slab. After the sample is homogeneous, a sample is printed using a mold made of Teflon in accordance with the standard of Basic Laboratory of Universitas Airlangga. Teflon rings with a thickness of 8 mm and a diameter of 8 mm for testing physical and mechanical properties. Testing this sample requires a flat surface by leveling it using a cement spatula or plastic filling instrument and placing the load on the Teflon ring so that it is solid as shown in Figure 1. After hardening the next 15 minutes the sample can be removed from the Teflon ring. Samples were made in 4 pieces and can be tested mechanically and physically.

Table I: Sample Composition

Sample	Sample Variation % Al2O3	Volume Fraction ZnO (%)	Volume Fraction ZnAl2O4 (%)	Volume Fraction Al2O3 (%)
A	24	79,5	20,5	-
B	26	74,18	23,51	2,31
C	28	68	25,3	3,7
D	30	69,55	27	3,45

Figure 1: Samples

X-Ray Diffraction (4XRD) Test

Characterization by XRD aims to determine the composition of the sample forming material and analyze the crystal phase. This test is carried out in the ITS energy laboratory. X-ray is an electromagnetic radiation with a wavelength ($\lambda \approx 0.1$ nm) which is shorter than the wavelength of visible light (λ = 400 - 800 nm) (5). Characterization with XRD PanAnalytical E'xpert Pro. Sample preparation for XRD characterization can be carried out as follows. First the sample is crushed until smooth. Then the sample which has become a flat surface powder is placed on the preparation. The preparations are then placed in the X-ray diffractometer holder sample and irradiated with X-rays at an angle of 2θ. The data generated from XRD characterization is a continuous spectrum that describes the angles of diffraction occurring in the atoms of material (2θ), the magnitude of the relative intensity produced (I / Io) from the distance between fields (d). Then the diffraction

data is recorded and recorded by a computer in the form of peak intensity graphs. Analysis of the XRD data spectrum can be done using the search match program International Centre for Diffraction Data (ICDD). By matching the peaks according to the XRD graph in the test sample.

Compressive strength Test

Compressive strength is the capacity of a material or structure to withstand loads tending to reduce size, as opposed to which withstands loads tending to elongate. The tool used is Shimadzu autograph AGS-10kNX with crosshead speed 0.001 to 1000 mm/min This strength test is carried out using cylindrical shaped samples. Data obtained from experiments are the diameter of the sample and the force required to suppress the sample.

Surface Hardness Test

The measurement of the level of surface hardness of a dental cement sample is performed using a Micro Vickers Hardness test. The angle of pyramidal diamond indentor is 136°. The level of hardness is measured in three different places, namely the right, left and center of the test material. The sample used is cylindrical.

RESULTS

X-Ray Diffraction (4XRD) Test

The results of the analysis by XRD is a diffractogram in the form of a line or peak arrangement with different intensities and positions specific to the material being analyzed. This experiment was related to the application of X-rays to determine the phase formed and the percent of volume phase fraction formed in the dental powder of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) with the addition of Aluminum Oxide (Al_2O_3). Figure 2 is the XRD test results of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) powder with Al_2O_3 filler.

XRD characterization in Figure 2 shows the diffraction patterns in each sample. The resulting pattern has almost the same shape in all samples. The difference is seen in the percentage of compound phase volume fraction formed in each sample. The results of the characterization are shown in Table II. It appears that the most dominant phase table formed after the sintering process was Zinc Oxide (ZnO). The characteristic of ZnO is that it is not dissolved in water and alcohol, but is dissolved and dissolved in most types of acids such as hydrochloric acid and has a fairly strong stability. Zinc Oxide (ZnO) has a hexagonal crystal structure with cell parameters a = b = 3.249 and c = 5.205. The XRD test results show the volume fraction of $ZnAl_2O_4$ in samples C and D has increased.

Compressive Strength Test

The graph of the relationship between the compressive strength values of dental cement Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) with the variation

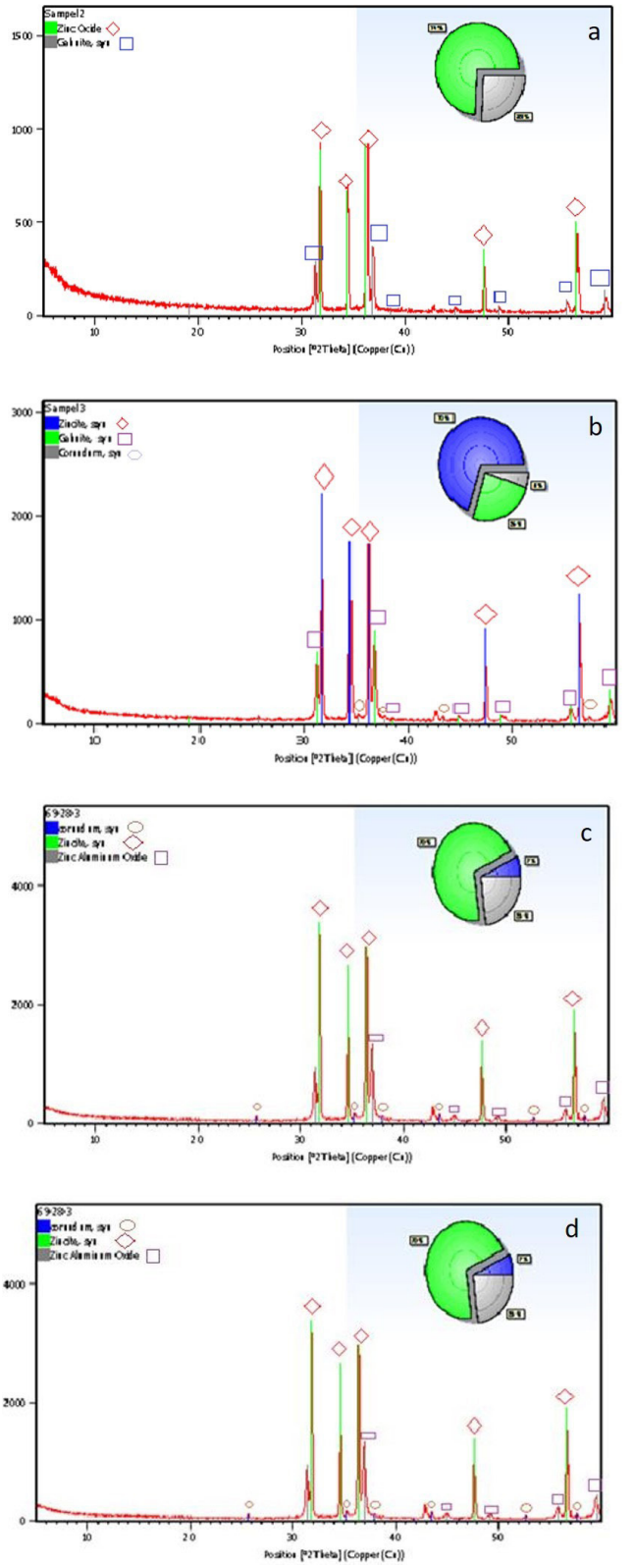

Figure 2: XRD result of dental cement ZOE-EBA with filler Al2O3 (a) filler Al2O3 24%, (b) filler Al2O3 26%, (c) filler Al2O3 28%, (d) filler Al2O3 30 %

of weight percent Al_2O_3 is presented in Figure 3. In the compressive strength test results, sample A has a compressive strength value of 40.8 MPa. Sample B has a compressive strength value of 64.49 MPa. Sample C has a compressive strength value of 37.61 MPa and Sample

Table II: Volume Fraction Samples

Sample Type	Concentration of Al_2O_3	Composition of ZnO:Al2O3:MgO	Solvent
A	24 %	73:24:3	Eugenol + EBA 37,5% + 62,5%
B	26 %	71:26:3	
C	28 %	69:28:3	
D	30 %	67:30:3	

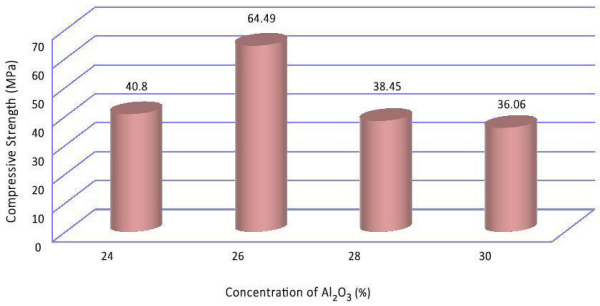

Figure 3: The Compressive Strength Result of ZOE-EBA Dental Cement

D has a compressive strength value of 39.6 MPa. The highest compressive strength value is found in sample B with a percentage of Al_2O_3 weight of 26%, which is 64.49 MPa.

Hardness Test

Data obtained from the results of the hardness test in the form of violence (VHN). Value of compressive strength of dental cements Zinc Data obtained from the results of hardness test in the form of hardness value (VHN). The graph of the relationship between the hardness value of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) and weight percent Al_2O_3 is presented in Figure 4. On the results of the hardness test, sample A with percentage of Al_2O_3 weight of 24% has a hardness value of 49.46 VHN. Sample B with percentage of Al2O3 weight of 26% has highest hardness value of 69.33 VHN. Sample C with percentage of Al2O3 weight of 28% has a hardness value of 44.16 VHN and Sample D with percentage of Al2O3 weight of 30% has a hardness value of 38.33 VHN. The highest hardness value is found in sample B with a heavy percentage of Al2O3 as much as 26%, 69.33 VHN. The value of violence increases with increasing weight percent of Al2O3, but the addition of Al2O3 is 28% and 30% the value of violence decreases.

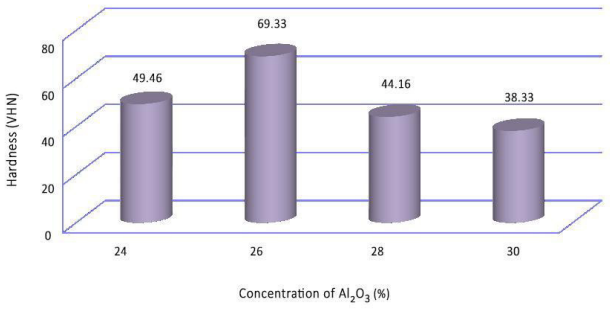

Figure 4: The Hardness Result of ZOE-EBA Dental Cement

DISCUSSION

X-Ray Diffraction (XRD) Test

The greater the percentage of $ZnAl_2O_4$ volume fraction will reduce the mechanical properties of dental cement because the greater the $ZnAl_2O_4$ volume fraction, the $ZnAl_2O_4$ distribution of the dental cement powder of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) will be in homogeneous thereby causing the density of dental cement samples to decrease. Because the sample density will affect its density, where the density will affect the mechanical properties (8).

Another compound formed from this dental cement powder is Zinc Aluminum oxide ($ZnAl_2O_4$). The properties of $ZnAl_2O_4$ include high mechanical resistance, high thermal stability, and low surface acidity (9). Zinc Aluminum oxide ($ZnAl_2O_4$) has a face-centred-cubic crystal structure (10).

Table II is the result of the volume fraction of a dental cement powder sample after the sintering process. These results indicate that ZnO is the dominant constituent element. To increase powder density, the sintering process is carried out, because in the sintering process there is a thermal treatment and a diffusion process occurs(11). Al_2O_3 compounds react with ZnO to form $ZnAl_2O_4$. The $ZnAl_2O_4$ compound is formed through the sintering process of the ZnO and Al_2O_3 reactions ZnO(s)+ Al_2O_3 (s) → $ZnAl_2O_4$ (s)

The best result is in the sample B (percentage of Al_2O_3 26%) with lowest volume fraction Al_2O_3 which is 2,31. The more percentage of the volume fraction of $ZnAl_2O_4$, the $ZnAl_2O_4$ distribution of the ZnO matrix is not homogeneous, so that the density of dental cement decreases and causes its porosity to increase (12). Porosity occurs due to different shapes of $ZnAl_2O_4$ powder and ZnO powder.

Compressive Strength Test

On the addition of Al_2O_3 by 28% and 30% the compressive strength value decreased. Increased compressive happened at 24 to 26% only. Decreased compressive strength due to the saturation point with the addition of excess Al_2O_3. The XRD test results show the volume fraction of $ZnAl_2O_4$ in samples C and D has increased. The greater the percentage of $ZnAl_2O_4$ volume fraction will reduce the mechanical properties of dental cement. This is because the porosity increases so that the density of dental cement decreases (12). With the formation of many porosity (pore), the sample density will decrease, this is due to the lack of homogenization in the sample so that more pores are created. Compressive strength standard values of dental cement Zinc Oxide Eugenol-Ethoxy Benzoic Acid

(ZOE-EBA) of 40 Mpa (13). In the XRD test the volume fraction of $ZnAl_2O_4$ in samples C and D has increased. The greater the percentage of $ZnAl_2O_4$ volume fraction will reduce the mechanical properties of dental cement because the greater the $ZnAl_2O_4$ volume fraction, the $ZnAl_2O_4$ distribution of the dental cement powder of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) will be inhomogeneous thereby causing the density of dental cement samples to decrease. The sample density will affect its density, where the density will affect the mechanical properties (14). This is related to the nature of $ZnAl_2O_4$ which has high mechanical resistance so that it can cover the fragile properties possessed by ZOE-EBA dental cement. On the addition of Al_2O_3 by 28% and 30% the compressive strength value decreased. Decreased compressive strength due to the saturation point with the addition of excess Al_2O_3. Saturation point is the point at which a substance will receive no more of another substance in solution, chemical combination (15). The XRD test results show the volume fraction of $ZnAl_2O_4$ in samples C and D has increased. The greater the percentage of $ZnAl_2O_4$ volume fraction will reduce the mechanical properties of dental cement. This is because the porosity increases so that the density of dental cement decreases (12). In addition, the compressive strength value of dental cement samples is also influenced by the addition of Ethoxy Benzoic Acid (EBA) liquid. Mixing dental cement powder with Ethoxy Benzoic Acid (EBA) liquid will produce a stronger crystal matrix, which is salt crystal, so that it can affect the nature of dental cement (7).

Hardness Test

Sintering at a temperature of 1000°C degrees is intended to form a new crystal phase, namely $ZnAl_2O_4$, It is intended that the grains (grains) in adjacent particles can react and bind. In this process there will be an increase in cohesion between the constituent particles and compaction through the elimination process of porosity. This process is an irreversible thermodynamic process to change a collection of unstable particles to be more stable. On the addition of Al_2O_3 by 28% and 30% the compressive strength value decreased. Decreased compressive strength due to the saturation point with the addition of excess Al_2O_3. The XRD test results show the volume fraction of $ZnAl_2O_4$ in samples C and D has increased. The greater the percentage of $ZnAl_2O_4$ volume fraction will reduce the mechanical properties of dental cement. This is because the porosity increases so that the density of dental cement decreases (12). The value of hardness in large molars is 63.73 VHN, small molars 60.17 VHN and series are 63.33 VHN (16). The hardness value of ZOE-EBA tooth cement with the addition of 26% Al_2O_3 of 69.33 VHN is close to the value of hard molars of 63.73 VHN.

The XRD test results show the volume fraction of $ZnAl_2O_4$ in samples C and D has increased. The volume fraction is obtained from the equation : $n\lambda = 2\ d \sin \theta$. And from the test results that came out through the XRD test. The greater the percentage of $ZnAl_2O_4$ volume fraction will reduce the mechanical properties of dental cement because the greater the $ZnAl_2O_4$ volume fraction, the distribution of $ZnAl_2O_4$ to the Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) powder will not be homogeneous, causing the density of dental cement samples to decrease. The density of the sample will affect its density, where the density will affect the mechanical properties (17). Vice versa, the smaller the percentage of volume $ZnAl_2O_4$ the mechanical properties of dental cement will decrease.

CONCLUSION

The addition of Aluminum Oxide (Al_2O_3) concentration in the manufacture of Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) cements had an effect on structural properties and physical properties. The XRD characterization results showed that a new compound was formed, namely Zinc Aluminum oxide ($ZnAl_2O_4$). The percentage of $ZnAl_2O_4$ volume fraction is getting bigger with increasing Al_2O_3 concentration. Physical properties were shown from the compressive strength and hardness test decrease in line with increasing Al_2O_3 concentration. The concentration of Aluminum Oxide (Al_2O_3) which gives the best characteristics for dental cement, Zinc Oxide Eugenol-Ethoxy Benzoic Acid (ZOE-EBA) is at a concentration of 26% due to the lowest volume fraction Al_2O_3 which indicate that the sample more homogenous and more dense.

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REFERENCES

1. Notohartojo, Indirawati T dkk. Nilai Karies Gigi Pada Karyawan Kawasan Industri Di Pulo Gadung Jakarta.Media Litbang Kesehatan.2011. Vol. 21. No.4. pp:166-167.
2. Anusavice, J.K. Philips: Buku Ajar Ilmu Kedokteran Gigi. Alih Bahasa: Johan Arif Budiman dan Susi Purwoko.Jakarta. E.GC. 2003.
3. Abdillah, Moh eza, dkk. Laporan Tutorial Skenario III Blok Bahan dan Teknologi Kedokteran Gigi II Semen Kedokteran Gigi. Universitas Jember: Jember. 2011. pp: 2-6.
4. Arthur J. Nowak, Tad R. Mabry, Martha H. Wells, John R. Christensen, Janice A. Townsend. Pediatric Dentistry, Infancy Through Adolescence, 6th Edition, 2019, Elsevier BV, 293-303
5. John A. Tesk, Joseph M. Antonucci, Clifton M. Carey, Fred C. Eichmiller, J. Robert Kelly, Nelson W. Rupp, Richard W. Waterstrat, Anna C. Fraker,

Lawrence C. Chow,Laurie A. George, Gary E. Schumacher, Jeffrey W. Stansbury, Edward E. Parry. Dental Materials, 2002. Wiley Online Library, https://onlinelibrary.wiley.com/doi/full/10.1002/0471238961.0405142020051911.a01

6. McCabe, J. F, Applied dental materials. 2008. 9th ed, Blackwell Pub, Walls, Angus, Oxford, UK.
7. Brauer GM, McLaughlin Richard, Huget EF. Aluminum Oxide as a Reinforcing Agent for Zinc Oxide-Eugenol-o-Ethoxybenzoic Acid Cement. Journal of Dental Research. 1968. Vol. 47 No.4pp: 622-625.
8. Hariyana, Agus M. Rancang Campur Beton Ringan dengan Agregat Ringan Plastis Berdasarkan Metode SNI 03-3449-2002. 2008. Skripsi Departemen Sipil, Fakultas Teknik UI: Depok
9. L. Gama, M.A. Ribeiro, B.S. Barro, R.H.A. Kiminami, I.T.Weber, A.C.F.M.Costa. Synthesis and characterization of the NiAl2O4, CoAl2O4 and $ZnAl_2O_4$ spinels by the polymeric precursors method. Journal of Alloys and Compounds. 2009. 483. pp: 453–455.
10. Suresh, et al. Electronic structure of spinel oxides: zinc aluminate and zinc gallate. J. Phys.: Condens. Matter 11 (1999) 3635–3644. Printed in the UK Department of Physics, Michigan. Technological University. Houghton, MI-49931: USA.1998. pp: 3635-3636.
11. Zuraidawani Che Daud, Shamsul Baharin Jamaludin. The Effect of Sintering on The Properties of Power Metallurgy (PM) F-75 Alloy. Advanced Materials Research Vol 795(2013), 573-577.
12. Ruwaida, Fauziati A dkk. Sintesis MMCs Cu-Al_2O_3 Melalui Proses Metalurgi Serbuk dengan Variasi Fraksi Volume Al2O3 dan Temperatur Sintering. Skripsi Fakultas Teknik Material Dan Metalurgi ITS: Surabaya. 2011. pp: 6-8.
13. Baum L, Phillips R W, Lund MR. Ilmu Konservasi Gigi 3rd ed. Alih Bahasa Rasinta Tarigan. Jakarta:EGC. 1997.
14. Hariyana, Agus M. Rancang Campur Beton Ringan dengan Agregat Plastis Berdasarkan Metode SNI-03-3449-2002. Skripsi Departemen Sipil, Fakultas Teknik
UI: Depok, 2008.
15. https://www.dictionary.com/browse/saturation-point
16. Maria del Pilar Gutiйrrez-Salazar, Jorge Reyes-Gasga. Microhardness and Chemical Composition of Human Tooth. VMoalt.e r6ia, lNs Ro.e s3e,a 2rc0h0, 3Vol. 6, No. 3, 367-373, 2003.
17. Shohana Iffat. Relation Between Density and Compressive Strength of Hardened Concrete. Concrete Research Letters, Vol. 6(4) 2015