RESEARCH ARTICLE OPEN ACCESS

A novel approach of synthesizing 2-hydroxyethyl methacrylate embedded hydroxyapatite composites for dentistry applications

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ABSTRACT
This research focused to find out chemical and structural suitability of novel Hydroxyapatite composite synthesized using Chloroapatite and 2-hydroxyethyl methacrylate as Dental filling material. For that, Solid State Sintering technique was used to produce Hydroxyapatite using Sri Lankan Chloroapatite and Calcium hydroxide. After reinforcing it with 2-hydroxyethyl methacrylate, physical and chemical properties were examined via comparing and contrasting it with the human tooth and commercially available Glass Ionomer cement (GIC), used in the field of Dentistry. Results show there is a close similarity between the synthesized product and the human tooth. Therefore, the study concluded that synthesized Hydroxyapatite composite can be used directly as a substitution for commercial dental filling material.

Keywords - Dental fillings, Dentistry, Human tooth, Hydroxyapatite, 2-hydroxyethylmethacrylate

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DATE OF SUBMISSION: 01-04-2019 DATE OF ACCEPTANCE: 15-04-2019

I. INTRODUCTION

Eppawala Chloroapatite Deposit is one of the nonrenewable phosphate sources situated in Anuradhapura, ancient capital of Sri Lanka which usually contains 34-40% total phosphorus expressed as percentage of Phosphorus pentoxide (P_2O_5).[1-5] Among so many phosphate products, up to the date Eppawala Chloroapatite mineral is only considered as the raw material for fertilizer industry. Therefore, we have value added Eppawala Choloroapatite into Solid State Sintered Eppawala Hydroxyapatite (SSHAp), a form of Hydroxyapatite, using solid state sintering method, considering its ability to replace chlorine with other groups at high temperature due to the increase of reactivity as its chlorine positions are under strain in the structural framework .[2, 3]

Hydroxyapatite is a widely used bioceramic which has a close chemical and structural similarity with human hard tissues and performs several outstanding properties biocompatibility, non-inflammatory in nature, osteoconductivity, non-toxicity, bioactivity etc. [6-11] As a result it has a range of biomedical applications mainly in the fields of orthopedics and dentistry.[12-25] 2-hydroxyethyl methacrylate is a widely used desensitizing agent which prevents excitation of the tooth nerve and relieves pain caused by tooth hypersensitivity. It use in adhesives, sealant chemicals, intermediates and for producing resins for paint/coating etc. [26]

Association of two different materials can lead to new materials, often called 'Composites' with higher properties or combination of each material property. Therefore, here in this study our aim is to reinforce synthesized SSHAp using 2-hydroxyethyl methacrylate resin monomer to increase its biomaterial properties as a ceramic composite and to find out it's structural suitability for dentistry applications mainly as a dental filling material focusing Non stress bearing restorations, Deciduous teeth restorations, Geriatric restorations, Intermediate restorative and base material for cavities using sandwich technique, Cervical restorations, Cold build ups, Temporary fillings and Dentine replacement etc. For that we have compared and contrasted it with human tooth as well as commercially available Glass ionomer cement, which is currently used for dental applications in Sri Lanka.

Selected commercial product also contains Fluoroaluminosilicate glass with 2-hydroxyethyl methacrylate polymer and it is currently used as self-curing conventional glass ionomer restorative material in Sri Lankan government hospitals which indicates for Non stress bearing restorations, Deciduous teeth restorations, Geriatric restorations, Intermediate restorative and base material for cavities using sandwich technique, Cervical restorations, Cold build ups, Temporary fillings and Dentine replacement etc. It is prepared directly before use by mixing its powder component with

polymer component clinically and resulted paste is cured within a few seconds. [27]

II. METHODOLOGY

2.1 Sample preparation

Natural raw apaptite mineral were collected from the Eppawala Apatite site. Then they were sorted as High Grade Rock Phosphate by the visual appearance of less coated apatite. After removing mud, collection of Apatite rocks were dried under sunlight, crushed using a jaw Crusher (Serial no: 1720011, China) into small crystals /powder, grind further into micron/Nano level HERP powder using a planetary Ball Mill (XQM – 4.0A) and sieved using sieve set (A060_01AC/0219, Scotland). Less than 63 micron range particle size powder were collected and oven dried at a temperature less than 150 ^{0}C for 5 hrs to prepare Moisture Removed HERP powder (MHERP). MHERP was taken as the raw material for synthesizing Hydroxyapatite. Samples were prepared using Solid state sintering technique as mentioned bellow. MHERP powder was added with needed weight of $Ca(OH)_2$ powder, after well mixing, sieving and high temperature heat treating Solid State Sintered Eppawala Hydroxyapatite powder (SSHAp) was synthesized according to following equation. [2,17]

$$Ca_{10}(PO_4)_6Cl_{2(s)} + Ca(OH)_{2(s)} \xrightarrow[\Delta]{<1800\ ^0C,\ (8\text{-}10)\ hrs} Ca_{10}(PO_4)_6(OH)_{2(s)} + CaCl_{2\ (s)} \quad (1)$$

Then the synthesized ceramic powder was mixed with commercially available 2-hydroxyethyl methacrylate polymer until a paste forms. As the second step, commercial cement powder and 2-hydroxyethyl methacrylate were mixed together to prepare a paste.

2.2 Sample characterization

Before mixing with the polymer, Commercial GIC powder and Eppawala Hydroxyapatite was examined under X-ray fluorescence Spectroscopy (Rigaku XRF Spectrometer) to find out its elementary composition and presence of impurities. The polymer was identified using Fourier Fourier Transform Infrared Spectroscopy (Bruker – Alpha FTIR Spectroscopy) under ATR technique. Then the mixtures of newly synthesized product and commercial product along with the human bone were characterized using XRD, FTIR, TGA, and SEM with EDS techniques. The crystallographic phases of samples were determined by X- ray diffractometer (Rigaku – Ultima. IV diffractometer) in reflection mode with Cu Kα1: 0.154 nm radiation.1.50 min^{-1} scanned speed was used to collect data within 2θ range from 15^0 to 80^0. The presence of functional groups was confirmed by FTIR over the region 400-4000 cm^{-1} using KBr pellet technique. The resolution of the spectrometer was 4 cm^{-1}. The surface morphology and microstructural features of samples were studied using Hitachi SU6600 Analytical Variable Pressure FE-SEM (Field Emission Scanning Electron Microscope) and Oxford Instruments EDX with AZtec software. Furthermore, Thermogravimetric analysis (TGA) was done using a Thermal Analyzer (SDT Q600) with N environment, 10 ^{0}C min^{-1} heating rate, and 1450 ^{0}C maximum temperature to find out the thermal stability of samples.

III. RESULTS AND DISCUSSION

Synthesized Solid State Sintered Eppawala Hydroxyapatite (SSHAp) powder contains Ca, P and O include in higher weight percentages and Fe, Al and Si as the impurities with hexagonal crystal structure showing a close similarity with mammalian bones and consists of many correlated, microcrystalline structures/particles/ spherulites with micro pores while credenting good thermal stability. [2,17] Table 1 confirms that Commercial Glass Ionomer Cement sample contains Al and Sr in higher amounts and S, Fe, Ca and Ba in less amounts as mentioned in the literature.

TABLE 1: XRF results for Commercial Glass Ionomer Cement

Element	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %
13 Al	49.46	42.39	43.03	45.82	43.29	43.13
16 S	0.30	-	-	-	-	0.25
20 Ca	0.48	0.35	0.39	0.32	0.31	0.30
26 Fe	0.23	0.17	0.20	0.17	0.18	0.20
38 Sr	49.34	56.79	55.36	53.29	55.94	55.87
40 Zr	0.19	0.20	0.27	0.28	0.27	0.16
56 Ba	-	0.10	0.74	0.12	-	0.08

TABLE 2: SEM with EDS results for Solid state product with polymer mixture, commercial GIC with polymer mixture and Human tooth

Element	Solid state sintered product with polymer mixture			Commercial GIC with polymer mixture			Human Tooth		
	Spot 1 Wt %	Spot 2 Wt %	Spot 3 Wt %	Spot 1 Wt %	Spot 2 Wt %	Spot 3 Wt %	Spot 1 Wt %	Spot 2 Wt %	Spot 3 Wt %
O	58.4	60.0	60.1	53.5	57.4	57.0	63.7	58.3	49.2
C	16.0	17.0	17.2	13.8	17.3	17.1	19.4	14.9	7.4
Ca	18.1	15.8	15.9	-	-	-	10.2	17.3	28.9
P	6.7	6.4	6.2	0.8	0.5	0.5	5.2	8.8	13.8
Cl	0.7	0.7	0.6	-	-	-	-	-	-
Al	-	-	-	7.3	5.1	5.2	0.3	-	-
Fe	-	-	-	-	9.8	-	0.2	-	-
Sr	-	-	-	7.2	4.8	4.9	-	-	-
Si	-	-	-	6.4	4.3	4.4	0.5	-	-
Na	-	-	-	1.0	0.8	0.7	0.3	0.3	0.7
F	-	-	-	9.8	-	10.1	-	-	-
Co	-	-	-	0.1	-	-	-	-	-
Mg	-	-	-	-	-	-	0.2	0.4	-

Table 2 describes the results of SEM with EDS analysis for Solid state sintered product mixture, commercial product mixture and human bone. According to that; SEM with EDS images of SSHAp with polymer mixture show that sample contains O, Ca in higher amounts and then P, C, Cl in order. Fe also found in very less amount as an impurity. Commercial product mixture contains O, C presence in higher amounts of the products and in order F, Al, Sr, Si, N, P and negligible amount of Ca. Human tooth contains O presence as the highest amount and then C, Ca, P and Si in order. Na, Al, Fe, Mg presence in very fewer amounts. When comparing results, it can be stated that a human tooth and the mixture of SSHAp with polymer have similarity in composition.

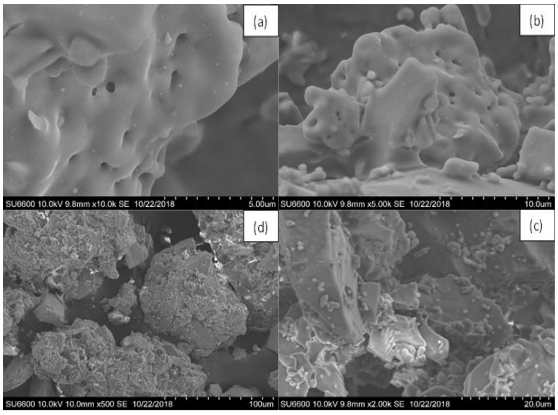

Figure 1: SEM images for SSHAp with polymer mixture, 10.0 kv, a) 10K b) 5KX c) 2KX d) 500X

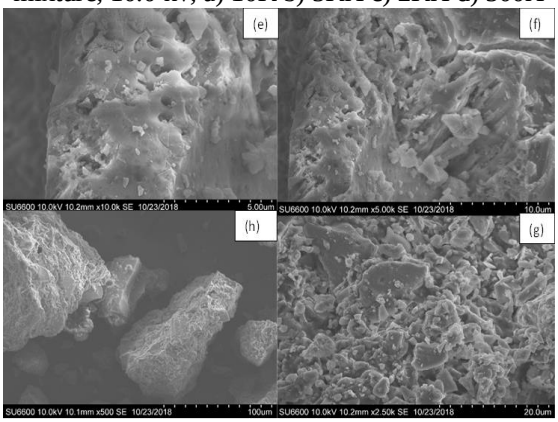

Figure 2: SEM images for Commercial GIC mixture, 10.0 kv, e) 10K f) 5KX g) 2. 5KX h) 500X

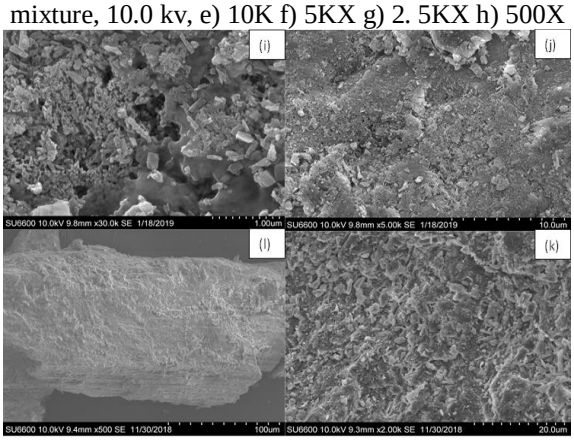

Figure 3: SEM images for Human Tooth, 10.0 kv, i) 30K j) 5KX k) 2KX l) 500X

SEM images of all mixtures and human tooth including Figure 1-3; show that there are good correlations of particles. SSHAp with polymer and human tooth only carried out micropores as shown in the Figure 1 Porosity would be helpful for tooth ingrowth as well as for good blood circulation to the tooth. According to Figure 3, some crystalline property can be found only in human tooth sample.

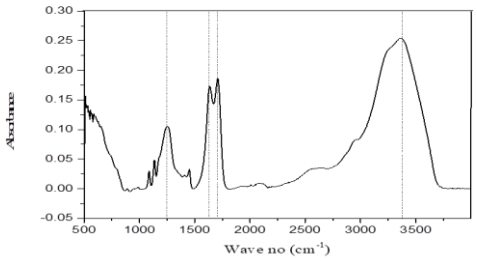

Figure 4: FTIR graph for polymer

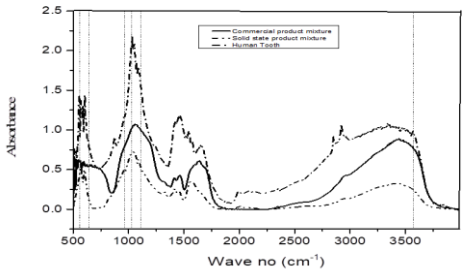

Figure 5: FTIR comparison for Commercial GIC with polymer mixture, SSHAp with polymer mixture, and Human Tooth

Figure 4 shows the resulted graph for polymer it has coincided with the FTIR characteristic graph for 2-hydroxyethyl methacrylate, interpreting several peaks related to stretching vibrations including a sharp intense peak at 1731 cm^{-1} related to the presence of ester carbonyl group, broad peak nearly 1150 cm^{-1} due to the C-O (ester bond) and a peak nearly 1250 cm^{-1} is due to the vibrations of C-C bond. Also literature shows the broad peak ranging from (3000-3500) cm^{-1} is owing to the presence of stretching vibration.[26] As shown in the Figure 5, all peaks for phosphate groups in the 560 $cm^{-1,}$ 640 cm^{-1}, 963 cm^{-1}, 1028 cm^{-1} and 1110 cm^{-1} wave no range and Characteristic peak for OH^-/ Hydroxyapatite nearly 3572 cm^{-1} wave no appeared in the Human Tooth as well as the SSHAp with polymer mixture.[2,17] It confirms that even after the mixing, the presence of Hydroxyapatite in the SSHAp product. When considering Commercial product mixture, it shows peak nearly 3572 cm^{-1} wave no range, which may due to the presence of OH^- group, but that couldn't be identified as Hydroxyapatite characteristic peak, as no peaks found related to phosphate groups. Apart from that, some peaks can be found commonly in both commercial product mixture and SSHAp mixture except in Human Tooth nearly (750 cm^{-1}- 2000 cm^{-1}) wave no range and 3000 cm^{-1} wave no range which is also appeared in Figure 4, they are the related peaks for 2-hydroxyethyl methacrylate. As a result it can be concluded that both commercial product and SSHAp mixed well with the polymer.

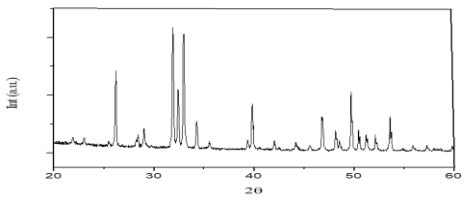

Figure 6: XRD pattern for SSHAp with polymer mixture

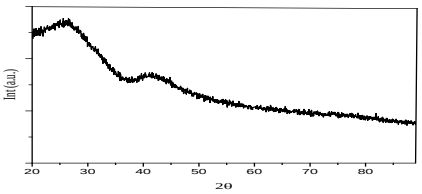

Figure 7: XRD pattern for Commercial GIC with polymer mixture

Figure 6 explains even after mixing 2-hydroxyethyl methacrylate polymer, XRD results of SSHAp mixture all characteristic peaks related to the crystallographic phases 002, 210, 211, 112, 300, 202, 310, 222, 213 and 004 of hexagonal Hydroxyapatite, which shows similarity to Human Tooth.[2,17,28,29] Comparing those results with Figure 7, XRD pattern for Commercial GIC with polymer it has carried out an amorphous structure without crystalline properties.

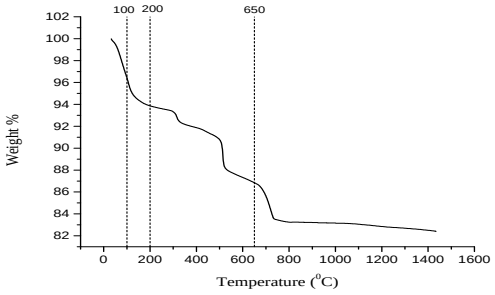

Figure 8: TGA curve for SSHAP with polymer mixture

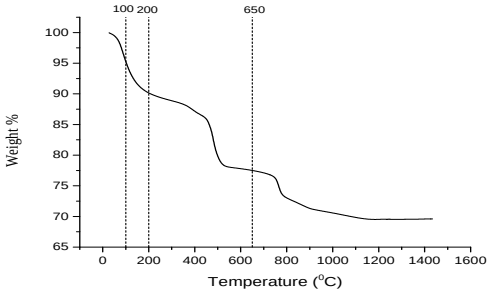

Figure 9: TGA curve for Commercial GIC with polymer mixture

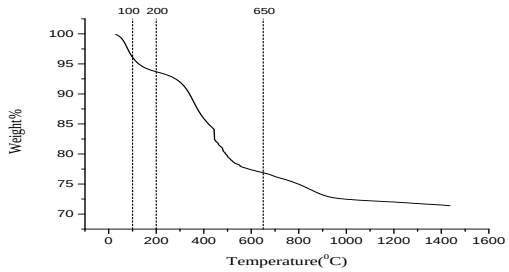

Figure 10: TGA curve for Human tooth

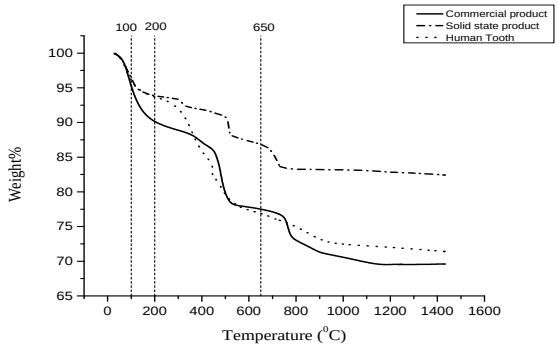

Figure 11: Comparison between TGA results of Human Tooth, Commercial product mixture, and Solid state product mixture

14.4850 mg of SSHAp with polymer mixture was subjected to TGA as shown in the Figure 8. First significant weight loss which occurs in between 0 ^{0}C- 250 ^{0}C (0.9201 mg) representing 6.352 %, may associate with the dehydration of the sample. Then again up to 400 ^{0}C, 0.2505 mg weight loss indicating 1.73% occurred and following that interval, the sample reduced its weight nearly 4.653%, 0.6740 mg at 750 ^{0}C; they may occur due to the gas elimination. Then again from 750 ^{0}C to 825 ^{0}C there is a weight loss indicating 4.01% (0.5818 mg) which has occurred due to the incipient transformation of produced Hydroxyapatite in β – TCP. Therefore, it indicates the formation of Hydroxyapatite in products. At 1432.97 ^{0}C 82.45 % of the original weight has remained.

As figured in Figure 9, 14.7280 mg commercial product mixture was subjected to TGA. First significant weight loss which occurs in between 0 ^{0}C- 250 ^{0}C (1.626 mg) representing 11.04 %, may associate with the dehydration of the sample. Then again up to 500 ^{0}C, 1.628 mg weight loss indicating 11.06% was taken place, it may occur due to the gas elimination. Following that, some weight losses occur in between small intervals indicating 7.019 % of initial weight (1.034 mg) 765 ^{0}C to nearly 950 ^{0}C, 1.342% of initial weight (0.1977 mg) 950 ^{0}C to 1200 ^{0}C those may occur due to the structural deformation and elimination of some gaseous compounds with different molecular weights. At 1434.27 ^{0}C 69.60 % of the original weight has remained.

According to the Figure 10, 14.3800 mg Human Tooth sample was subjected to TGA. As mentioned in the literature; first significant weight loss which occurs nearly at 200 ^{0}C (0.9166 mg) representing 6.374 %, may associate with the dehydration of the sample. Following that interval the sample reduced its weight nearly 3.378 mg at 650 ^{0}C; it has occurred due to the tooth structure collagen elimination. This reaction continues up to 1100 ^{0}C, with a lowered rate. Above that temperature, a fine TGA curve descending slope is observed up to maximum analyzed temperature of 1436.52 ^{0}C with the total weight loss of 28.60%, this being associated with the collagen remains removal & the incipient transformation of Hydroxyapatite in β – TCP. [2,17, 28,30]

When comparing Human Tooth with Commercial GIC with polymer mixture and SSHAp with polymer mixture, according to Figure 11, all three samples have shown the relatively same pattern of weight loss. But due to the composition similarity, weigh losing pattern have a similarity 650 ^{0}C to 1430 ^{0}C temperature range of Human Tooth and SSHAp with polymer mixture than the commercial product as they were containing Hydroxyapatite. Also due to the least amount of weight loss in synthesized SSHAp mixture sample than Tooth and commercial product mixture, it can be concluded that the synthesized SSHAP with polymer mixture perform high thermal stability and good material stability in nature and application.

IV. CONCLUSION

Study concludes that synthesized material consists of less than 50 micron range particles and has a close chemical and structural similarity with Human Tooth. Also it performs high thermal stability and good material stability in nature. Therefore, it can be used as a direct substitution for dental filling material.

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R.D. Gunaratne" A novel approach of synthesizing 2-hydroxyethyl methacrylate embedded hydroxyapatite composites for dentistry applications" International Journal of Engineering Research and Applications (IJERA), Vol. 09, No.04, 2019, pp. 51-57