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Original Article

Synthesis and Characterization of Hydroxyapatite from Biowaste for Poly (methyl methacrylate) Composites

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Abstract – *The aim of this work is to determine the chemical composition of hydroxyapatite (HAp) and evaluate the stress at the onset of plastic deformation and how quickly heat spreads through poly (methyl methacrylate) (PMMA) Composites. Sixteen samples of heat-cured PMMA were filled with snail shell hydroxyapatite (SHAp) and periwinkle shell hydroxyapatite (PHAp). Isopropyl tri (dioctyl pyro phosphate) titanate was used as a coupling agent on the hydroxyapatite. The HAp was synthesized by hydrothermal synthesis, and the PMMA samples were produced by the casting method followed by compression and curing. Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) spectroscopy was used to characterize the HAp, and Universal Testing Machine and Modulated Differential Scanning Calorimeter were used for Yield Strength (YS) and Thermal Diffusivity (TD) analysis of the PMMA composites, respectively. Design-Expert software using the optimal mixture design of experiment (OMDOE) method was used to design and analyze the YS and TD of the PMMA composites, with $p < 0.05$ considered statistically significant. The ratio of calcium/phosphorus (Ca/P) was 1.70 for PHAp and 1.60 for SHAp. The YS is between 19.04 and 48.06 MPa, and the TD is between 9.07 X 10^{-7} and 2.39 X 10^{-7} m^2/s. The highest mechanical and thermal properties were obtained when PHAp and SHAp were combined, showing a synergistic property of the HAp.*

Keywords - *Composite materials, Dental implant, Dental restoration, Thermal diffusivity, Yield strength.*

1. Introduction

PMMA is a dominant acrylic that is widely used to produce partial and complete dentures [1]. It is widely used in orthopedic applications, bone fillers, bone substitutes, etc. [2]. It gained significant attention in various industries because of its outstanding properties and ease of processing [3]. PMMA offers inherent advantages such as ease of handling, cost-effectiveness, and injectability [4]. It was observed that PMMA is the most suitable for denture base [5].

PMMA has some disadvantages, which include high polymerization temperature, high elastic modulus, high compressive strength, etc. To improve these mechanical properties, several studies have modified PMMA by adding bioceramics, bioglass, polymer materials, nanomaterials, and other materials [4]. The mechanical properties of dentures can be improved by reinforcing with rubbers, fillers, and fibers [1]. Calcium β-pyrophosphate was used to fill PMMA for dental applications. It was observed that there was a significant improvement in mechanical properties, while there was a slight improvement in thermal stability [6].

PMMA is limited due to a lack of capacity for bone regeneration. PMMA/HAp has good bioaffinity properties, is biocompatible with bone cells and has fairly good compressive strength. It was observed that the addition of HAp nanoparticles at different loadings resulted in improvement in the mechanical properties of the denture [7]. The filling of HAp with PMMA was proposed to have good physical properties, good compressive strength, good bioaffinity properties, biocompatible with bone cells, etc. [8]. The Ca/P ratio for HAp was 1.70 [9], while the Ca/P ratios for HAp were 1.57, 1.67 and 1.87 [10]. And HAp was dominant for Ca/P ratio of 1.60 [11].

The prediction of PMMA crack patterns is important to control the total damage to the denture [12]. The denture base is subjected to various stresses during its function [13]. Data of PMMA crack trajectories were analyzed to predict the crack propagation pattern and use the results of the experimental data to develop a numerical model to study crack patterns. Research has, however, suggested that light-cure PMMA used as restorative resin decreased viable cell numbers and cell

proliferation and damaged cell membranes [14]. Hence, heat-cure PMMA are preferable in dental applications due to their superior colour stability, low cost, light weight, etc. [15], [16].

The impact of incorporating Gadolinium oxide nanoparticles into heat-cured acrylic denture materials was assessed, the glass transition temperature was evaluated using a differential scanning calorimeter, and the result revealed significant improvements in glass transition temperature [17]. The temperature dependence of human enamel and dentin on the specific heat capacity (SHC) was shown at a temperature range of 20 ^{0}C to 70 ^{0}C using differential scanning calorimetry, where the SHC increased with temperature [18]. The thermal diffusivity of PMMA filled with aluminum powder was evaluated from measurements of a temperature range of 100 to 370 K, and the behavior was correctly predicted by the Hashin-Shtrikman relationship based on variational principles and within Nielsen's model [19]. The thermal diffusivity of PMMA/PC blend was analyzed using a Differential Scanning Calorimeter, and it was observed that the thermal diffusivity was decreased with an increase in temperature up to 450 to 460 K [20].

The experimental designs for mixtures are useful tools for studying the effects of ingredients/components in formulations, and optimal design of experiments has the capacity to provide good estimates of the parameters with the use of minimal resources [21], [22]. These optimal designs derived from the Pareto front facilitate the experimenters to select the most suitable design based on their priority using the desirability function [23]. It was concluded that the use of smart design of experiment tools has the capacity to reduce experimental testing, thus saving resources compared to the old use of deploying the one-factor-at-a-time method of design [24].

There is limited information on PMMA/HAp composite utilization as a dental implant fixture. To the best of our knowledge, little or no experimental studies have been conducted on the use of the OMDOE method to evaluate the stress at the onset of plastic deformation and how quickly heat spreads through PMMA filled with HAp. This study aims to fill this gap by using the OMDOE method to evaluate these properties of PMMA filled with HAp.

2. Materials and Methods

Periwinkle and snail shells were acquired, washed, dried, crushed and calcined in a muffle furnace (Infitek Co. Ltd., Minhang, Shanghai, China) at 900 ± 5 ^{0}C for six hours. The calcined powder was allowed to rest in a damp environment for about four hours to imbibe moisture. The powder is then reacted with phosphoric acid (Molychem, Mumbai 400002, India) according to the stoichiometry of their reaction. And ammonium hydroxide solution (Molychem, Mumbai 400002, India) is used to keep the reaction mixture in alkaline region, that is pH of 9 ± 0.1, the beaker containing the mixture is placed on magnetic stirrer (Zenith Lab Co. Ltd., Jincheng, Jintan, China) and the temperature is placed at 80 ± 5 ^{0}C for two hours.

The powder is removed and subjected to heat in oven for three hours at 180 ± 5 ^{0}C, it is allowed to cool and washed severally with distilled water, then it is placed in oven at 110 ± 5 ^{0}C for two hours to dry and sterilize before analyzing the HAp with scanning electron microscope-energy dispersive xray (Jeol Limited, Tokyo, Japan) to determine the identity, quantity and chemical composition of the HAp samples. Design-Expert software (11th edition, Stat-Ease Inc., USA) was deployed for the design using the OMDOE method. 16 groups were designed for yield strength and thermal diffusivity properties analysis of the PMMA composites.

The samples were cast on a denture flask using the formulation in Table 4. Isopropyl tri (dioctyl pyro phosphate) titanate (Capatue Chemical, Nanjing, Jiangsu, China) was used as a coupling agent on the HAp. Mixing was done until the dough stage was reached, and the dough was packed into the mould for curing. The mould is closed, compressed by a manual hydraulic press (Henan Chuanghe Lab. Equipment Co. Ltd., Zhengzhou, Henan, China) and inserted into a water bath (Infitek Co. Ltd., Minhang, Shanghai, China). Curing is followed for 30 minutes at 100 ± 2 ^{0}C.

The mould is left to cool in the water bath for 30 minutes. The composite is left to cool on the bench at room temperature, and the mould is subsequently opened. The composite is incubated in distilled water at 37 ± 2 ^{0}C for 48 hours for conditioning before testing. Universal testing machine (Laizhou Jin Cheng Co., Limited, Laizhou, Shandong, China) and modulated differential scanning calorimeter (TA Instruments, Delaware, USA) were used to determine the yield strength and thermal diffusivity properties of the PMMA composites, respectively.

The data were analyzed with Design-Expert software using the OMDOE method. The $p < 0.05$ was considered statistically significant. The coefficient of determination (R^2), F-values, and p-values of the independent variables on the dependent variables were obtained from the Fit statistics and one-way ANOVA. The analysis was conducted using an in vitro technique.

3. Results and Discussion

Table 1 is the SEM-EDX analysis result for PHAp; the atomic concentrations for Ca and P are 18.52 and 10.89, respectively. Therefore, the ratio of Ca/P is 1.70. Table 2 shows the SEM-EDX analysis result for SHAp; the atomic concentrations for Ca and P are 22.13 and 13.82, respectively, and the ratio of Ca/P is 1.60. These results agree with the studies of [25] and [26].

Table 4 shows the formulation, YS, and TD of the PMMA composites; the YS values are between 19.04 MPa and 48.06 MPa, while the TD have values of 9.07 X 10^{-7} m^2/s to 2.39 X 10^{-7} m^2/s. These YS values are in agreement with those of [27] and [28]. Table 3 is the ANOVA and fit statistics result; a linear model was used for YS. The (F-value = 4.68) shows that the factor (independent variable) is statistically significant, and a (p-value = 0.0294) indicates that it is significant, since (p-value < 0.05), and the confidence interval is above 97.06 %. The multiple correlation coefficient (R^2 = 0.4186) indicates 41.86 % of the variance in the response variables was explained by the model, while the adequate precision of 5.7749 shows that the values are desirable. Reduced special quartic model was used to analyze TD, where the (F-value = 3.47) and the (p-value = 0.0463), hence F-value and p-value are statistically significant, as the (p-value < 0.05). Moreover, the confidence level is above 95.37 %. The (R^2 = 0.6983) shows that 69.83 % of the variance in the response variables was explained by the model.

Table 1. SEM-EDX analysis result for PHAp

Element Number	Element Symbol	Element Name	Atomic Conc. (at. %)	Weight Conc. (wt. %)
8	O	Oxygen	70.59	51.12
20	Ca	Calcium	18.52	33.61
15	P	Phosphorus	10.89	15.27

Table 2. SEM-EDX analysis result for SHAp

Element Number	Element Symbol	Element Name	Atomic Conc. (at. %)	Weight Conc. (wt. %)
8	O	Oxygen	64.04	43.79
20	Ca	Calcium	22.13	37.91
15	P	Phosphorus	13.82	18.30

Table 3. ANOVA and fit statistics result

Properties Analyzed	Model used	R^2	Adequate precision	F-value	p-value
Yield Strength	Linear	0.4186	5.7749	4.68	0.0294
Thermal Diffusivity	Reduced Special Quartic	0.6983	6.0445	3.47	0.0463

Note. R^2: multiple correlation coefficient

Table 4. Formulation, YS and TD of the PMMA composites

Run	PMMA wt. %	MMA wt. %	TCA wt. %	PHAp wt. %	SHAp wt. %	YS MPa	TD m^2/s X 10^{-7}
1	64	32	1.48	0.00	2.52	19.04	7.96
2	64	32	1.33	0.60	2.06	22.19	4.52
3	64	32	1.44	0.29	2.26	27.62	2.39
4	64	32	1.33	1.43	1.24	30.81	9.07
5	64	32	1.44	2.56	0.00	29.67	5.62
6	64	32	1.50	1.56	0.94	28.83	4.05
7	64	32	1.41	1.15	1.44	33.32	4.73
8	64	32	1.33	0.05	2.61	31.92	3.04
9	64	32	1.44	2.56	0.00	48.06	8.59
10	64	32	1.33	2.32	0.34	33.84	6.76
11	64	32	1.33	1.97	0.70	38.90	4.45
12	64	32	1.48	0.00	2.52	22.84	4.12
13	64	32	1.38	0.87	1.76	24.95	5.65
14	64	32	1.50	1.56	0.94	26.25	6.80
15	64	32	1.41	1.15	1.14	39.13	4.71
16	64	32	1.41	1.15	1.14	21.87	5.46

Note. YS: Yield strength, TD: thermal diffusivity, TCA: Isopropyl tri (dioctyl pyro phosphate) titanate, PMMA: poly (methyl methacrylate), MMA: methyl methacrylate model, while the adequate precision of 6.0445 shows that the values are desirable.

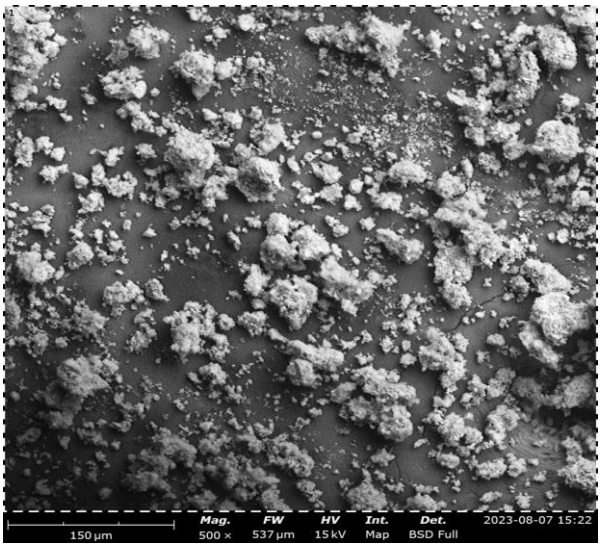

Fig. 1 SEM micrograph of PHAp

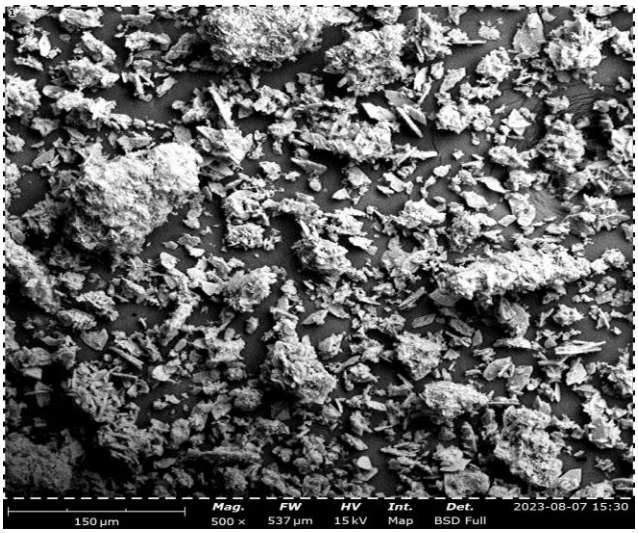

Fig. 2 SEM micrograph of SHAp

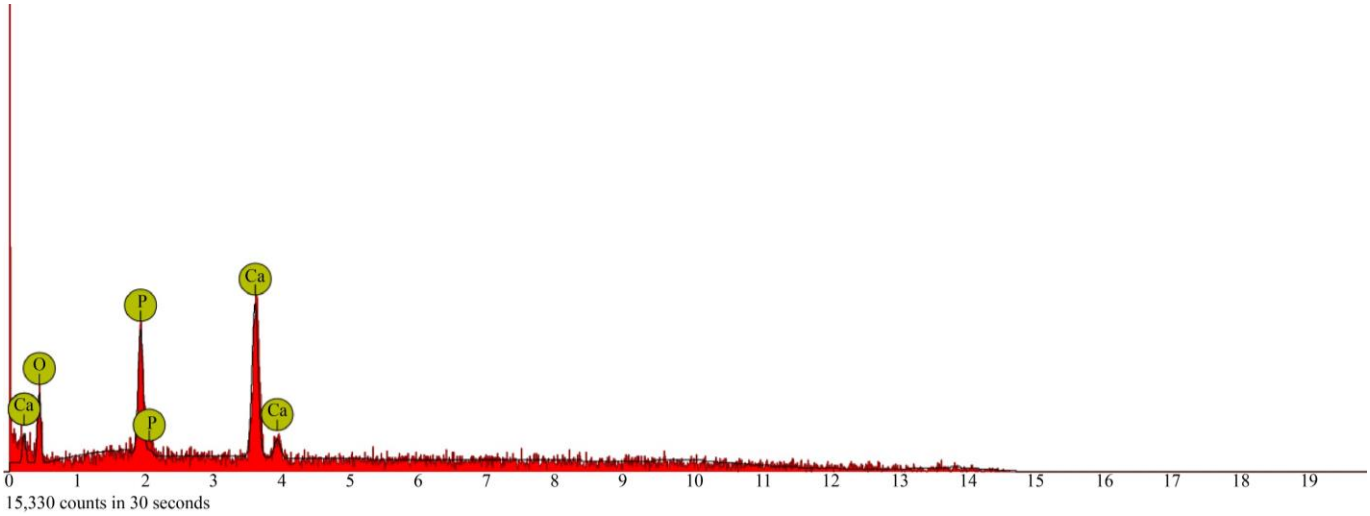

Fig. 3 EDX chart showing peaks for elements in PHAp

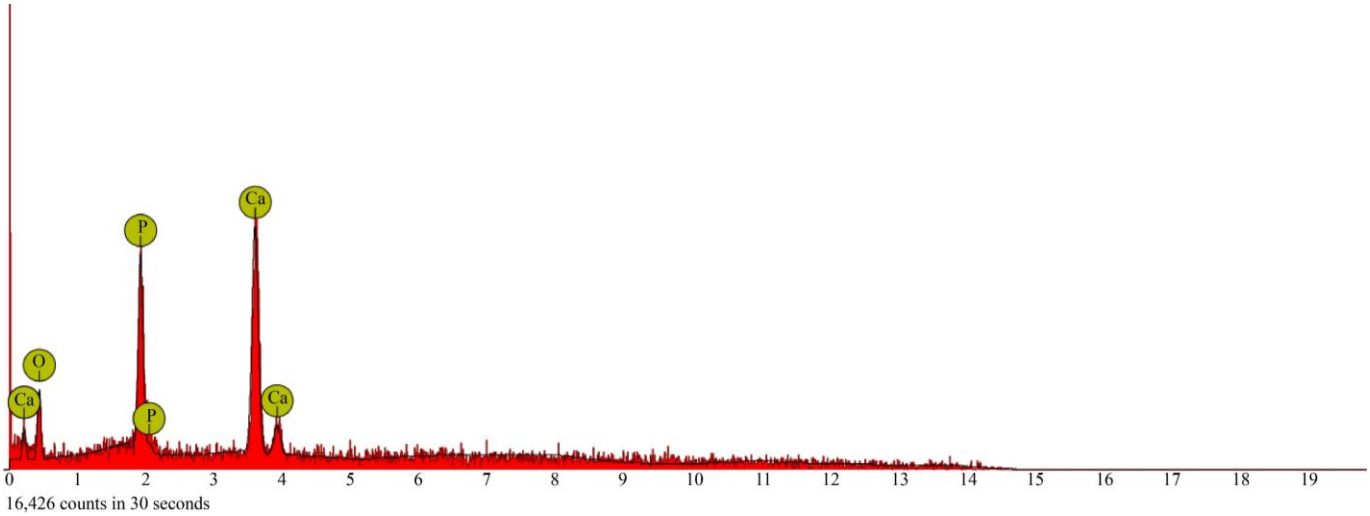

Fig. 4 EDX chart showing peaks for elements in SHAp

Figures 1 and 2 are SEM-EDX micrographs of PHAp and SHAp showing HAp agglomerate as a cluster of different sizes, while Figures 3 and 4 identify the peaks for calcium (Ca), phosphorus (P) and Oxygen (O). Hydrogen (H) was not identified by the SEM-EDX due to its light nature.

This study determined the chemical composition of hydroxyapatite (HAp) and evaluated the stress at the onset of plastic deformation and how quickly heat spreads through poly (methyl methacrylate) (PMMA) filled with HAp. The small sample size (N= 16) and the in vitro technique used limited the capacity to generalize the results. However, the use of modern analytical equipment by experts and the use of the OMDOE method extend the limitations of this research. Future studies may assess other properties of the composites, like biological properties, and the in vivo test method.

4. Conclusion

Within the limitations of this study, the SEM-EDX results suggest that the shell powders were hydroxyapatite (HAp), since the ratio of calcium/phosphorus (Ca/P) we obtained was 1.70 for the periwinkle shell hydroxyapatite (PHAp) and 1.60 for the snail shell hydroxyapatite (SHAp). HAp is predominantly present between Ca/P ratio of 1.60 to 1.70. The highest YS and TD values were obtained when both SHAp and PHAp were combined, suggesting a display of a synergistic property by the HAp. The ANOVA results revealed that the p-value and F-value were statistically significant for both YS and TD, R^2 of 0.4186 and adequate precision of 5.7749 for YS and R^2 of 0.6983 and adequate precision of 6.0445 for TD, indicating that the models are reliable, and the confidence interval is above 99.95 %, that is, p-value < 0.05. The valuable contribution of this paper is that the confidence interval is outstanding, which indicates that the data are reliable. Based on the above results, this composite will be of good use as a dental composite. More research is needed to optimize the outcome of this research, and in vivo clinical trials should be conducted to address some limitations of this study.

Data availability

Data will be made available by the corresponding author on reasonable request.

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