

RESEARCH PAPER

Mullite:PMMA Micro/Nano Composites Synthesized Using Solid State Reaction Method Used for Bone Substitutes

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ABSTRACT

Current paper displays a complete study into the synthesis of mullite bio-ceramics using a solid state reaction method and their combination into polymethyl methacrylate (PMMA) to improve mechanically matched biocomposites for bone and dental uses. Mullite samples (S1, S2, S3 and S4) were synthesized from a pure alumina and silica precursors and sintered at 1400°C. Phase evolution and microstructural characteristics were examined using X-ray diffraction and field-emission scanning electron microscopy, approving transformation into a stable orthorhombic mullite phase. Monolithic mullite presented high hardness values (up to 1388 MPa), significantly higher than those of human bone and dentin, which may induce stress shielding when used as an implant material. Four mullite:PMMA composites (C1, C1, C3 and C4) containing 10 wt.% ceramic reinforcement were synthesized. Combination of PMMA efficiently reduction of hardness to a biological range (111–150 MPa) while significantly increasing strain at failure (up to 0.15), closely to the mechanical characterization of human hard tissues. Bioactivity assessment using simulated body fluid showed the formation of hydroxyapatite on the surfaces. Depending on mechanical and biological investigations, composite C1 appeared as the suitable applicant for bone scaffold applications, while composite C2 showed more possible for dental uses.

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INTRODUCTION

The increasing request for biomaterials capable of replacing injured bone and dental tissues has increased studies into advanced bio-ceramics and polymer composites [1, 2]. The biomedical transplant material must show mechanical compatibility with natural tissues, adequate wear resistance and the ability to endorse biological combination [3]. Metallic implants often undergo from corrosion and elasticity misalliance, while ceramics deal chemical stability and wear

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resistance but are inherently brittle [4]. Alumino-silicate ceramics, mullite ($3\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2$) has attracted considerable attention due to its low thermal expansion, excellent chemical stability, and high resistance to creep and thermal shock [5, 6]. Whereas mullite has been broadly active in high temperature industrials, new researches show that controlled mullite microstructures may demonstration capable bio-compatibility [7]. Monolithic mullite has a extraordinary



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elasticity and fracture hardness leading to tension protective when implanted [8]. This phenomenon can constrain bone restoration and finally result in implant disappointment [9, 10]. An appropriate style to overcome this limitation contains amalgamation brittle ceramic with flexible polymers to made bio-composites in order to obtain a new composite with tailored mechanical properties [11]. Polymethyl methacrylate (PMMA) is one of the most commonly used polymer materials in bone and dental implantation applications due to its bio-compatibility and easy handling [12, 13]. Regardless of these compensations, Polymethyl methacrylate PMMA shows low wear resistance and undesired mechanical strength under high loading [14, 15]. Reinforcing PMMA with ceramic fillers such as mullite offers a good path to enhance mechanical characterizations, wear resistance, and biological performance [16, 17].

The present study aims to synthesize mullite ceramics using a solid state reaction method and advance Mullite:PMMA bio-composites with improved mechanical and tribological characterizations for biomedical applications. The correlation between ceramic composition, microstructure, mechanical response, and bioactivity is investigated to evaluate the

appropriateness of these composites for bone and dental substitutes.

MATERIALS AND METHODS

A pure alumina and silica powders were used as raw materials to synthesis four compositions (S1–S4) weighing the powders using a four digit analytical balance to obtain a total mass of 10 g per batch as shown in Table 1.

The mixtures were dissolved in deionized water for 48 hrs. to get a high homogeneity and to ease the particle diffusion during heat treatment. The suspensions were put on magnetic stirrer for 6 hours, and the pH was fixed at 9. The latter samples were dried at 100°C for 6 hrs. in a convection oven. The dried powders were calcined at 900°C for 2 hrs. to initiate the solid state reaction. The weights of the samples after calcination were (7.2, 7.6, 8 and 7.7 gm) for samples (S1, S2, S3 and S4) respectively. Then, a 1.5 gm from each powder was pressed into disc shaped pellets under a load of 12 tons for 1 min. Finally, these samples were sintering at 1400°C for 6 hrs. to achieve completely reacted mullite.

Mullite:PMMA composites (C1–C4) were synthesized by mixing 10 wt.% of mullite powders into a PMMA polymer (90 wt.%). The components

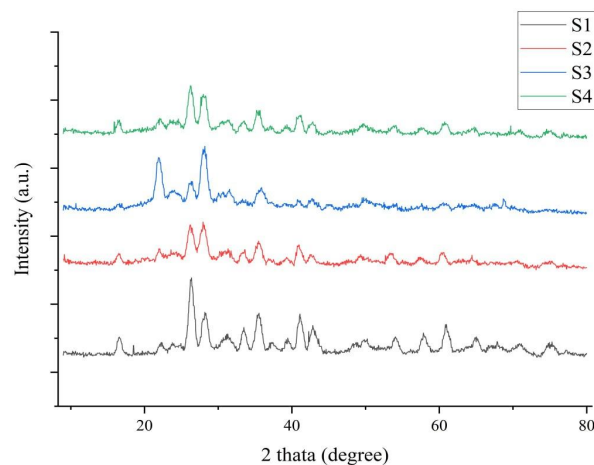


Fig. 1. XRD pattern for mullite sintered at 1400 °C for 6 hrs.

Table 1. Alumina and silica weight of samples S1, S2, S3 and S4.

Sample label	Alumina weight (gm)	Silica weight (gm)
S1	7.2	2.8
S2	5.3	4.7
S3	3.6	6.4
S4	6.3	3.7

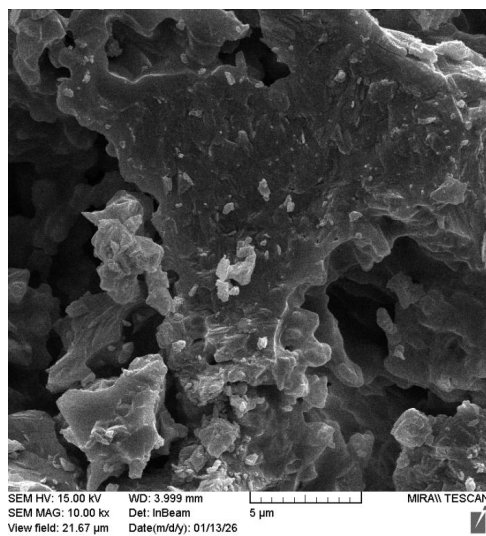
were carefully mixed to ensure highly dispersion and decrease agglomeration. Cylindrical samples with dimensions of 4 cm in length and 1 cm in diameter were prepared using hydraulic press.

The structure was investigated using X-ray diffraction (XRD, Panalytical) with Cu K α radiation. The microstructura were examined using field emission scanning electron microscopy armed with energy dispersive X-ray spectroscopy. Mechanical characterizations were evaluated using Vickers hardness testing and compression

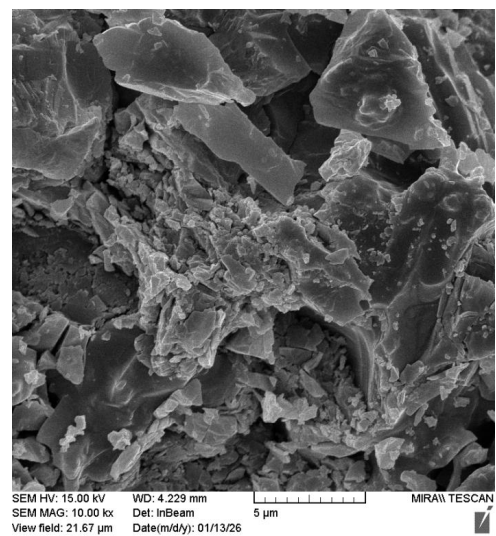
tests. Tribology behavior was measured under dry sliding situations using a pin-on-disc tribe-meter. The bioactivity was assessed by immersing samples in simulated body fluid, prepared according to Kokubo's protocol [18], at 37 °C for 40 days, and then structure analysis was carried out.

RESULTS AND DISCUSSION

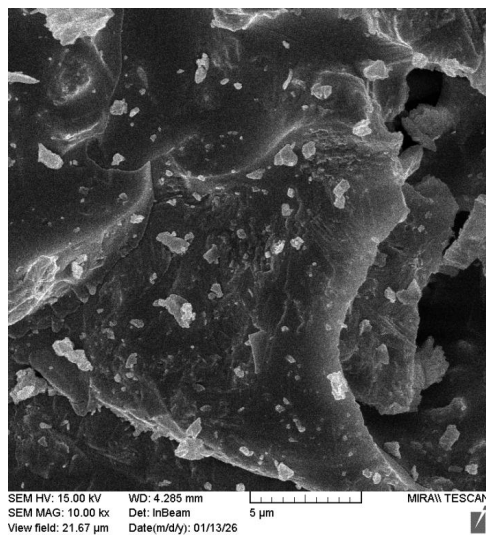
Fig. 1 displays XRD pattern of four pressed pellets mullite samples sintered in a thermal furnace at 1400 °C for 6 hrs.



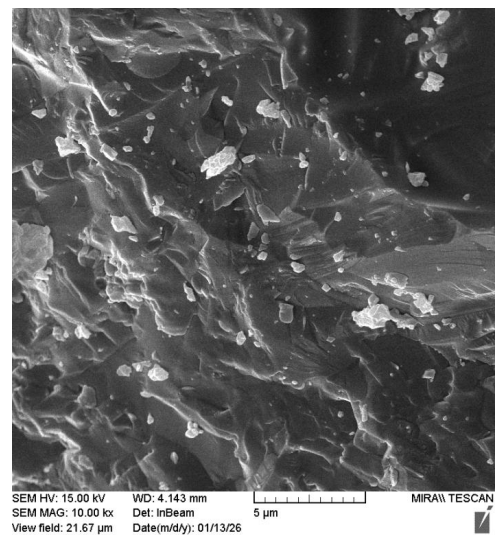
S1



S2



S3



S4

Fig. 2. SEM images of mullite samples sintered in at 1400 °C for 6 hours.

The XRD pattern of the pressed silica:alumina mixture sintered at 1400 °C for 6 hrs. shown a growth in phase composition and exhibits clear peaks at 2θ values around 16–17°, 25–26°, 33–35°, 40–41°, and 60°, which correspond to standard referee data for mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The augmented intensity and sharpness of the peaks may be designated that the mullite turns out to be the dominant crystalline phase at the greater sintering temperature. The amalgamation of raised up temperature and comprehensive soaking time is enhancing the solid state diffusion between alumina and silica which leading to the consumption of the initial oxide phases and forming of a thermodynamically stable mullite structure. When the powder mixtures were pressed into pellets previous to heat treatment improves powders particle contact and reaction homogeneity, which may be contributed to improved crystallinity and complete mullite

formation. These results agree with that reported in [19].

Fig. 2 shows the FE-SEM images of pellets mullite samples sintered in a thermal furnace at 1400°C for 6 hrs. synthesized using solid state reaction method.

These images demonstrated that the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratios are effect on the grain morphology. Compositions with high alumina displayed dense microstructures with quite equiaxed grains, while silica-rich compositions promoted anisotropic growing, resultant in extended rod mullite grains, forming interlocking networks that are probable to improve mechanical stability. The FE-SEM micrographs exposed that the microstructural morphology of the sintered mullite samples depends on the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio and that was demonstrated in [20].

EDX analysis confirmed the homogeneous distribution of Al, Si, and O within the samples as

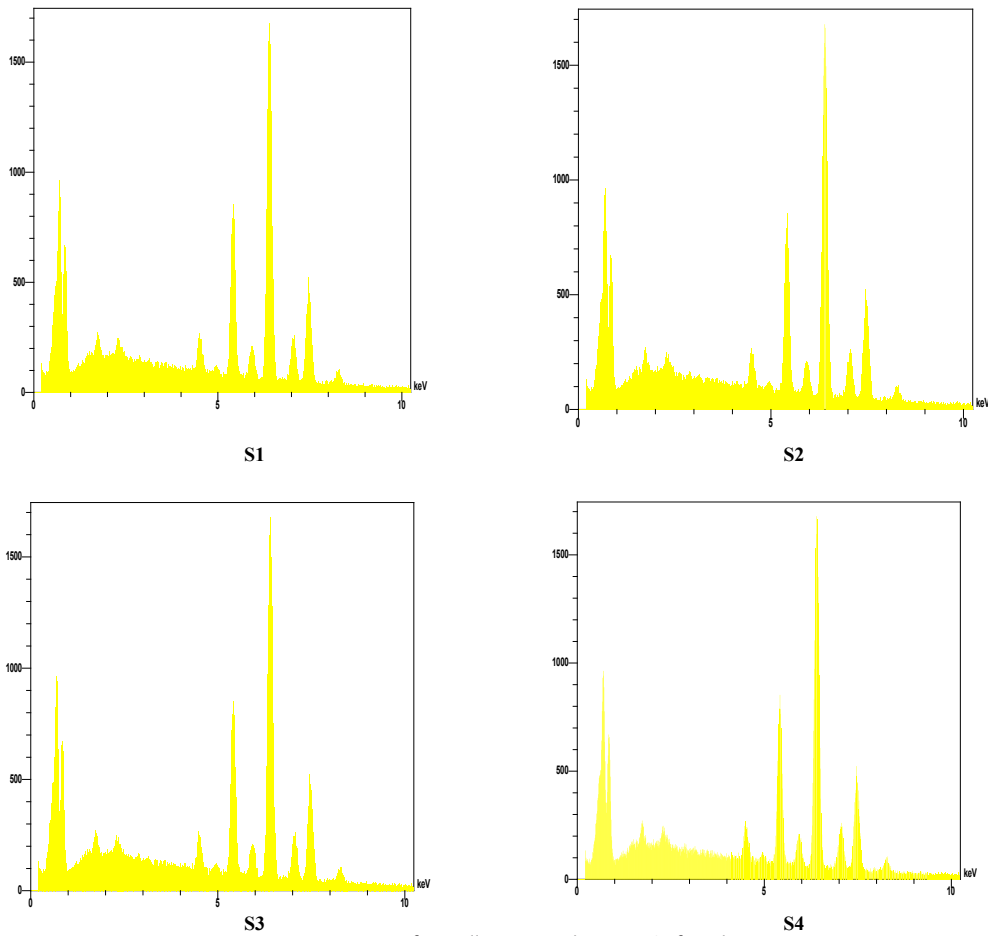


Fig. 3. EDX spectra for mullite sintered at 1400 °C for 6 hrs.

shown in Fig. 3.

The composition analysis diagnosed in EDX spectra indicates that the final mullite phase attituded the stoichiometric $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ratio with smallest noticed remaining both alumina and/or silica particles.

The atomic ratios of Al to Si expose the preliminary proportions of alumina and silica in each essential sample. Sample S1 exhibited a high Al:Si ratio as (4.16) consistent with its high ratio of alumina as was in starting mixture. While sample S2 showed a lower ratio (1.36), sample S3 had the lowest ratio (0.73) that reflecting a high silica content and sample S4 obtainable an intermediate ratio (1.24) indicating a more balanced Al:Si composition. These results authenticate that the final elemental distribution corresponds to the initial mixture and that homogenization and pellet pressing prior to sintering contributed to achieving uniform chemical composition of samples. The current results of EDS analysis were angered with the results that mentioned in [21].

The mechanical characterizations of mullite were listed in Table 2.

Obviously as shown in Table 2 that the Vickers micro-hardness exposes clear deviations in hardness among the synthesized mullite samples. Sample S1 showed the highest average hardness value (1388.35 MPa) signifying a denser and higher mechanical resistant compared to the other samples. While sample S3 showed the lowest average hardness (769.36 MPa) that may be attributed to higher porosity or less effective mullite formation. Sample S4 shown a relatively high average hardness; however, a major

distributing in individual hardness values was noticed ranging from 911.61 - 1599.11 MPa. This variation suggests micro-structural inhomogeneity possibly due to non-uniform grain size.

Samples S1 and S4 demonstrate the highest compressive strengths (1388 MPa and 1286 MPa) and high Young's modulus values (900–850 MPa) which reflecting their rigid and brittle nature. In contrast S3 shows lower compressive strength (769 MPa) with higher strain at failure (0.028) indicating greater flexibility under load. On the other side, S2 delivers a composed conduct with middle strength (1098 MPa) and adequate strain at failure (0.018). Mullite offers exceptional strength where its brittleness limit its application as a bone substitute making it more suitable for specialized dental components that require wear resistance rather than load bearing flexibility. The Vickers hardness results are closely to that polished in [22].

The mechanical characterizations such Vickers hardness, Young's modulus, compressive strength and strain at failure of mullite:PMMA composites were summarized in Table 3.

The final samples of mullite:PMMA composites showed a reduction with hardness in the range of 111–150 MPa aligning with human hard tissues. Compression exposed an alteration from brittle fracture in ceramics samples to ductile deformation performance in ceramic:polymer composites.

All mullite:PMMA samples display lower Young's modulus (120–140 MPa) and compressive strengths (111–150 MPa) compared to mullite, while strain at failure increases (0.12–0.15),

Table 2. Mechanical characterizations of mullite samples.

Sample	Average Hardness (MPa)	Young's Modulus (MPa)	Compressive Strength (MPa)	Strain at Failure
S1	1388.35	900	1388	0.012
S2	1097.58	780	1098	0.018
S3	769.36	550	769	0.028
S4	1286.39	850	1286	0.014

Table 3. Mechanical characterizations of mullite:PMMA composites.

Sample	Average Hardness (MPa)	Young's Modulus (MPa)	Compressive Strength (MPa)	Strain at Failure
C1	111	120	111	0.15
C2	150	140	150	0.12
C3	123	130	123	0.14
C4	147	138	147	0.13

showing an improvement in ductility. C1 reveals the highest strain (0.15) but lower strength (111 MPa), making suitable to applications needing flexibility. C2 displays the highest compressive strength (150 MPa) with a strain (0.12), shown a balance between rigidity and adaptability suitable for dental applications. So, the PMMA reduces

brittleness and distributes stresses regularly, result composites that are mechanically compatible with human tissues.

After 40 days of immersion in SBF, SEM and EDX analyses revealed the formation of calcium:phosphate layers on the mullite surfaces, characteristic of hydroxyapatite (HAp). Fig. 4

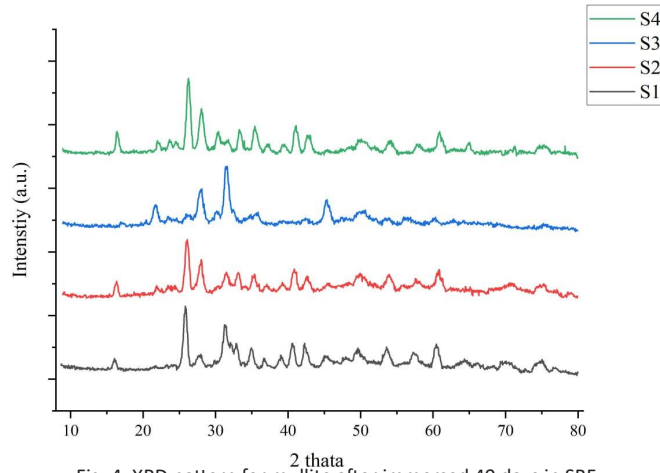
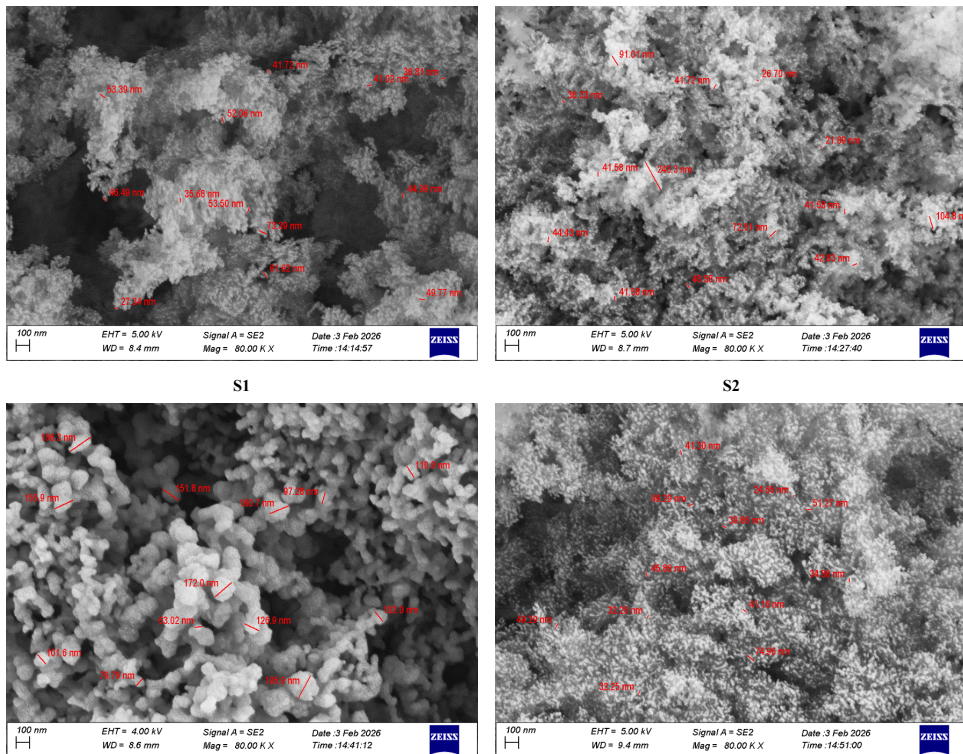


Fig. 4. XRD pattern for mullite after immersed 40 days in SBF.



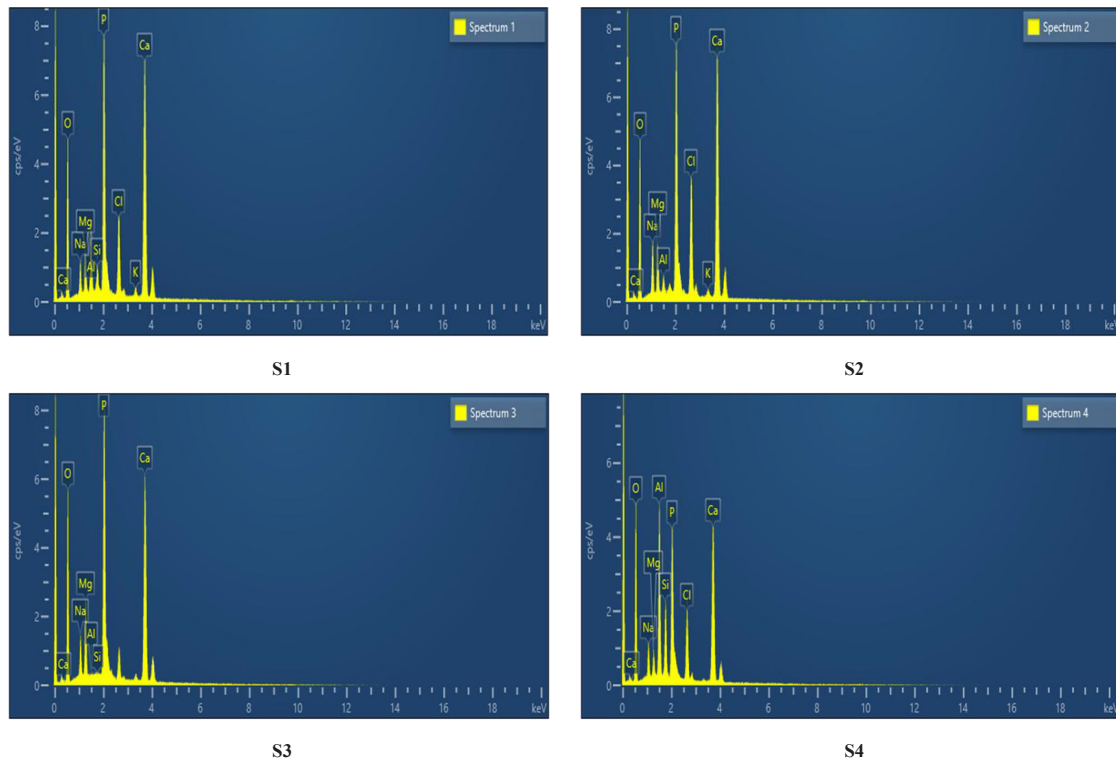


Fig. 6. EDX for mullite after immersed 40 days in SBF.

shows the XRD pattern for mullite after immersed 40 days in SBF.

Fig. 5 displays the SEM images for mullite after immersed 40 days in SBF for 40 days.

The SEM images showed formation of a cauliflower-like layer on the surface of the mullite. This layer is characteristic of HAp, the main component of natural bone. The morphology suggests that nucleation locations were provided by exposed mullite particles within the PMMA, which enabled apatite growth through ionic exchange between the SBF and the mullite surface.

Fig. 6 shows EDX for the mullite samples after immersing 40 days in SBF.

EDX results confirmed the existence of calcium and phosphorus in the formed layer, with a Ca:P atomic ratio approaching the stoichiometric value of HAp (1.67). The detection of oxygen supports the development of a mineral with phosphate. The homogeneous distribution of Ca and P observed in EDX indicates uniform bioactivity across the composite surface, suggesting that the combination of mullite improves nucleation and growth of HAp.

The comportment of mullite ceramics shows

that the mullite is capable for serving the surface mineralization that can support bone cell attachment in vivo. Ceramics phase existence is not individual provides nucleation locations but also releases both silica and alumina ions that can help to stimulate HAp formation that process can refine the osseointegration possible of these composites for orthopedic or dental applications.

CONCLUSION

Mullite ceramic materials synthesized using a solid state sintering reaction method at 1400 °C showed phase transformation and orthorhombic crystal structures. Though monolithic mullite has greater rigidity its direct use as a bone substitute is limited by mechanical unsuitability with human tissues. The composite of mullite: PMMA polymer effectively links this mechanical hole by reducing hardness, enhancing ductility and helping bio-activity. Among the enhanced composites, the sample C1 verified best strain tolerance making it a promising applicant for bone scaffold uses while the sample C2 exhibited a stable mechanical sample suitable for dental repairs. Immersion of the composite mullite:PMMA polymer into stimulated

body fluid for 40 days set their bio-activity. Both SEM and EDX results exposed the creation of a uniform HAP's layer on the composite surfaces signifying their capability to support mineralization and enhance osseointegration. This bio-activity combined with the mechanical characterizations which enhanced by adding the polymer. The combination of ceramic strengthening and polymer ductility together with confirmed in vitro bio-activity locations mullite:PMMA composites as candidates for bone and dental substitutes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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