

ORIGINAL ARTICLE

Synthesis and Characterization of Reinforced PMMA by Sol-gel Derived Functionalized Nano-porous Silica via In-situ Heat Polymerization Method for Denture Applications

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Abstract

Purpose: Polymethyl methacrylate resins are a class of materials used widely in dental practices. However, reinforcement of PMMA resins is the most important issue for the fabrication of overdentures/dentures with long-term durability. In the current study, the mechanical properties (in terms of tensile, bending, and impact properties) and applicability of the heat-polymerized Polymethyl methacrylate denture base materials were investigated by incorporating the synthesized sol-gel derived nano-porous silica aerogel.

Materials and Methods: Polymethyl methacrylate overdenture base materials were prepared by direct mixing of liquid MMA component with the desired weight contents of the synthesized sol-gel derived silica aerogel (i.e., 0, 2.5, 5, 7.5, and 10 wt%) followed by thermal polymerization. The mechanical properties of the prepared nano-composites were investigated in terms of tensile, impact, and bending strength, and the experimental results were also compared with those commercial Triplex Hot acrylic base overdenture resin.

Results: The experimental results revealed that there is a meaningful correlation ($P < 0.05$) between silica aerogel weight content and mechanical properties of the as-prepared silica aerogel- Poly-methyl methacrylate composites. Compared with commercial Triplex Hot base composite, fabricated Poly-methyl methacrylate base denture composites containing only 7.5 wt% of silica aerogel show higher mechanical properties. At optimum concentration, the bending, impact, and flexural properties of the composites reached 16.3 MPa, 22.9 MPa, and 38.1 KJ. m⁻², respectively.

Conclusion: The experimental results revealed that nano-porous silica aerogel is a promising alternative candidate to be used as an efficient filler in the fabrication of overdentures. Fabricated nano-composites using silica aerogel show higher mechanical properties, compared to fabricated commercial base composites. Furthermore, denture/overdentures had better fracture toughness by using nano-porous silica aerogel, and no more space is needed.

Keywords: Denture Bases; Silica Aerogel (Silicon Dioxide); Polymethyl Methacrylate; Composite Resin; Nano-composites; Biomedical; Dental Materials.

1. Introduction

From the 1940s, PMMA was considered the most popular and the main choice of materials for the fabrication of removable prosthetics and overdentures. Ease of processing, low cost of laboratory equipment and available materials, as well as the aesthetic appearance and high stability in the oral environment, are some main advantages of using PMMA composites in the field of dentistry. However, besides the great features, the manufacturing and serviceability of overdenture materials still suffered from poor mechanical properties of PMMA resin, including deformation and fracture of the denture base materials. It should be noted that fatigue and impact failure are two main reasons for overdenture fracture. The experimental investigations revealed that the fracture of overdentures/dentures occurs commonly due to heavy occlusal forces or accidental damage. Hence, manufactured implants cannot meet the required structural characteristics and they are suffered directly from occlusal forces such as fracture attachment, implant failure, and attachment dislodgement buffering. By improving the mechanical properties of acrylic resins with reinforcements, the required characteristic at low thickness could be available. In this regard, many attempts have been made to improve the mechanical properties of PMMA-based overdenture materials [1-4].

The recent experimental results show that compared with traditional reinforcements, the incorporation of nanomaterials can significantly enhance the mechanical properties of the fabricated dental PMMA-based nanocomposites at very low filler weight content. Zirconia (ZrO_2), alumina (Al_2O_3), titanium oxide (TiO_2) nanoparticles, as well as nano-size fibers are some well-known nanomaterials that are widely utilized in the reinforcement of PMMA composites [5-7]. El-Shennawy *et al.* [8] investigate the effect of TiO_2 nanoparticles (with different weight contents from 1 - 5 wt%) on the mechanical properties of two normal heat cures and high-impact acrylic base resins. The experimental results revealed that in all cases, utilization of 1 wt% of TiO_2 resulted in enhanced flexural (102 and 114 MPa) and impact strength (2.95 and 3.4 MPa). Farshid Sefat *et al.* [9] investigate the effect of surface modification on the mechanical properties improvement of

PMMA/micron-sized inorganic particles, including TiO_2 , SiO_2 , ZrO_2 , and Al_2O_3 . The experimental result revealed that in all cases, the PMMA fracture resistance was improved by silane modification of filler particles due to the uniform dispersion of reinforcements throughout the matrix. It should be noted that the effect of weight content variation on fracture toughness of the fabricated composites was not investigated. Arksornnukit *et al.* [10] investigate the effect of incorporation of silica nanoparticles on the mechanical properties of the fabricated PMMA/NP-silica nano composites. The experimental results show that utilization of 1% wt of surface-modified nano silica (optimum concentration) improved (~15%) the mechanical properties of the fabricated nano composites in terms of flexural strength and fracture toughness. Although many attempts have been made to improve the mechanical properties of the PMMA dentures using low-cost and available fillers, high cost of filler production, aggregation of nano size reinforcements, stress concentration, low interfacial bonding between fillers and matrix, and in some cases, biocompatibility are considered as the main drawbacks of nano-fillers utilization [11-13].

In the field of nano-engineering, recent experimental evidence reveals that the utilization of nanostructured (nano-porous) materials can significantly improve the mechanical properties of reinforced composites. Nanoporous materials are organic or inorganic-based substances with a meso/macropore size distribution. Zeolites, activated carbon, ceramics, inorganic porous hybrids, and aerogels/xerogels are some typical instances of this kind of natural or synthetic material [14-17]. Aerogels are a class of nanoporous substances, which can be prepared by the sol-gel process of both inorganic and organic precursors. Thanks to their valuable intrinsic properties, such as high porosity, high specific surface area, and tunable pore size distribution, these materials are used in various fields of engineering and medical applications. From biocompatibility point of view, silica aerogels/xerogels are sol-gel-derived materials formed in an open three-dimensional silica network with unique properties such as high specific surface area (800–1200 m^2/g), high porosity (~98%) and very low density (0.06 g/cm^3) [18, 19]. Due to the biologically inert properties of silica, it has been specifically exploited in engineering and medical applications, and it has received special attention for

the development of drug delivery, enzyme encapsulation, and mechanical improvement of implant composites [20-23]. Recently, Hegedus *et al.* [24] investigated the applicability of the bio-activated sol-gel-derived nano-porous silica in the field of dentistry. The analysis of osteogenic sarcoma cells shows that the bio-activated silica aerogel by hydroxyapatite can improve cell attachment. The behavior of osteosarcomas on both glass substrate and the modified silica aerogel was the same, indicating bio-activity and non-toxicity of silica aerogel for practical applications in the field of dentistry.

The main objective of the present study was to investigate the applicability of nanoporous silica aerogel as a new efficient filler to be used in the fabrication of denture bases with improved mechanical properties. The main idea for developing the current research is based on two hypotheses: first, due to the foam-like nature of silica aerogel and the regular arrangement of the silica species with a well-defined distance in the fractal structure, the possibility of better distribution of the reinforcement in the polymer matrix is higher. Second, due to the foamy nature of silica aerogel, PMMA-monomer can penetrate inside the silica pores and fill them. When the reaction starts, the polymerization will proceed from the inside to the outside of the silica pores, resulting in organic/inorganic interpenetrating networks that improve the connection between the silica particles as reinforcement and the polymer matrix, which can improve the mechanical properties of the final composites. Furthermore, due to the fractal-type structure of silica aerogel, the induced stress can propagate across the composite in three directions, improving the stress attenuation characteristic of the fabricated nano-composites. To achieve this goal, silica aerogel was prepared by using sodium silicate as a silica aerogel precursor through acid acid-catalyzed method, accompanied by chemical surface modification and ambient pressure drying. The reinforced PMMA base composites were prepared by direct mixing of liquid PMMA monomer with the desired weight contents of the synthesized silica aerogel (i.e., 0, 2.5, 5, 7.5, and 10 wt%) followed by thermal polymerization. The mechanical characteristics of the prepared composites were evaluated in terms of tensile strength, bending strength, and impact properties. The experimental results were also compared with commercial Triplex

hot PMMA resin. The analysis of the experimental results provided profound insight into the contribution of aerogels as filler to improving the mechanical properties of the fabricated PMMA base composites.

2. Materials and Methods

2.1. Materials

The materials implemented in the present study include sodium silicate (Si: Na mol ratio =3.33) as sol precursor, trimethylchlorosilane (TMCS) as chemical surface modifier, n-hexane (as solvent exchange agent), ethanol (as solvent), and Hydrochloric acid (HCl) as a sol-gel polymerization catalyst. Benzoyl peroxide, as a free radical polymerization initiator, was obtained from Merck and used as received. D.I. water was also used to prepare silica sol. For the sake of comparison, commercial Triplex Hot Resin was also used (Ivoclar Vivadent, Inc. LOT W86829). It should be noted that in all cases to obtain the MMA liquid component with triggered thermal polymerization characteristics, MMA monomer was mixed with benzoyl peroxide under the weight ratio of 99:1 prior to SiO₂-PMMA sample preparation.

2.2. Preparation of Silica Aerogel

Figure 1 shows a flowchart overview of the fabrication of hydrophobic silica aerogel. In a typical procedure, silica sol was prepared by mixing sodium silicate with the DI water to prepare a 12 wt% silica sol. After that, the desired amount of 1M HCl was added dropwise into the prepared silica sol to decrease the solution pH from 13 to 4. For gelation, the as-prepared silica sol was poured into an air-tight beaker and kept at room temperature. After gel formation, the prepared silica gels were aged in pure ethanol for 72 hr at a constant temperature of 30 °C. To improve the mixing of MMA with silica aerogel particles, chemical surface modification of the as-prepared silica wet gels is necessary. For this purpose, the as-prepared silica wet gels were immersed in TMCS/n-hexane (TMCS concentration of 15 wt% in n-hexane) solution for 24 hr at room temperature. Finally, the surface-modified wet gels were washed with fresh n-hexane and dried at 90 °C and 120 °C for 72 and 24 hr, respectively. Finally, to prepare PMMA/ silica aerogel composites, the synthesized silica aerogels were ground down and

sieved to obtain silica aerogel particles with a mesh size of 325.

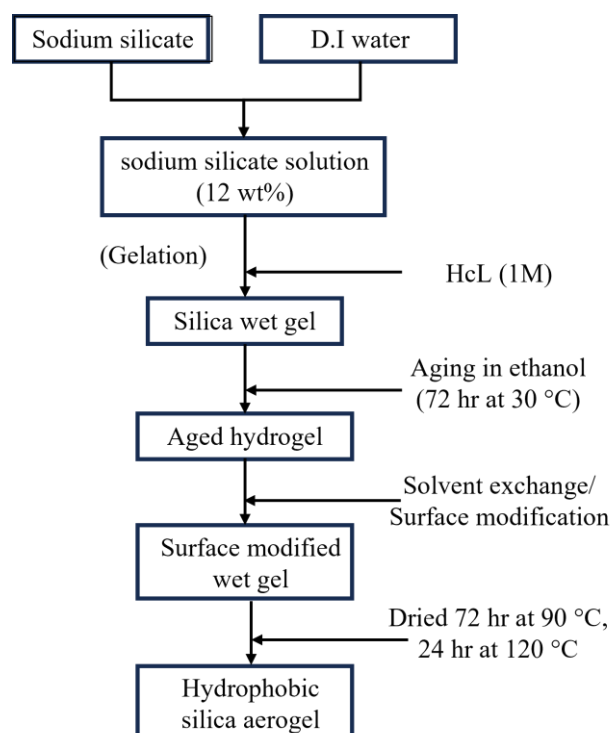


Figure 1. Schematic flow chart of the process for fabrication of hydrophobic sodium silicate-based silica aerogel

2.3. Composites Preparation

To investigate the impact of silica aerogel on the mechanical characteristics of the prepared composites, SiO₂-PMMA was prepared by the direct mixing of the grounded silica aerogel with the MMA monomer (under varied weight contents from 0 to 10 wt%), followed by thermal polymerization. For this purpose, the synthesized silica aerogel powder was well dispersed in the MMA monomer by using ultrasonication. It should be noted that, following impregnation of silica aerogel in MMA liquid, the silica aerogel's appearance changed from opaque to transparent characteristic, since liquid MMA monomer penetrated through silica aerogel pores and filled them. This phenomenon is due to the open-pore characteristic of silica aerogel. Hence, MMA polymerization proceeded from the inside to the outside of the silica pores, generating high-performance homogeneous organic-inorganic interpenetrating networks. Finally, the as-prepared mixtures were cast into the specific molds, according to ASTM sample dimensions, packed (using a 14 MPa

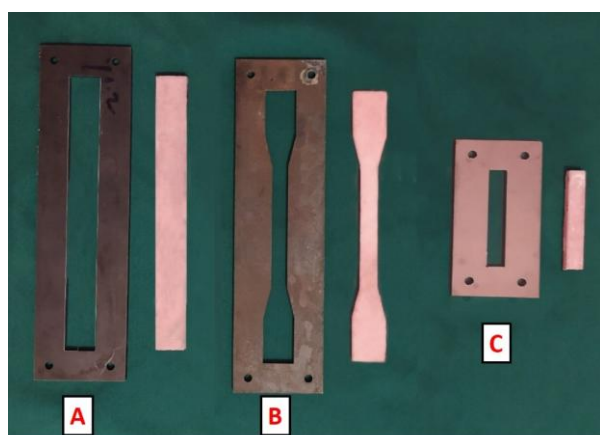
hydraulic press), and cured (polymerized thermally) in an oven. In all cases, thermal polymerization was performed for 6 hr at 70 °C, 3 hr at 90 °C, and 2 hr at 100 °C under standard laboratory procedure for preparing the nano-composites. Finally, based on the type of mechanical analysis, 3 main groups of SiO₂-PMMA nano-composites, each containing 0, 2.5, 5, 7.5, and 10 wt% of SiO₂ filler, were fabricated. Each subgroup also comprised 10 sample specimens, which were subject to mechanical characterization. For the sake of comparison, the commercial (Triplex Hot resin) PMMA denture composites were also prepared according to laboratory preparation instructions. The details of the prepared samples are presented in Table 1.

2.4. Characterization

The morphological properties of the samples were investigated by using field emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3 LMH/LMU). The chemical functional characteristics of the as-prepared samples were investigated by using FTIR spectroscopy (Bruker Equinox 55LS 101 series, Germany). The BET and BJH analyses were performed to estimate the specific surface area and pore characteristics of both the synthesized silica aerogel and the commercial Triplex Hot filler powders using Belsorp-mini (Nippon Bell, Japan). The mechanical properties of the prepared composites, including tensile strength, 3-point bending strength, and impact analysis, were performed according to ISO-527, ISO-178, and ISO-180, respectively. Tensile and bending strength analyses of the composites were performed by using a universal tensile test analyzer (GOTECH AL-3000). To do so, the dumbbell-shaped samples with the dimensions of 100*13*3mm were used for tensile and bending analysis, and the samples were fixed in a 50 KN load cell with a head speed of 20 mm/min. For impact analysis, the notched samples with the dimensions of 100*13*3 mm were used. The impact analysis of the prepared composites was conducted using a Charpy impact tester (Frank, Germany). Figure 2 represents the as-prepared composites for mechanical characterization.

Table 1. Details of PMMA/silica aerogel nanocomposites sample preparation

Main Groups	Subgroup	Description	PMMA/SiO ₂ (g)	NO. of samples
A (Impact strength test) (ISO-180)	A1	Commercial Triplex Hot base composite (For the sake of comparison)	-	10 Samples
	A2	Neat PMMA (control group)	100/0	10 Samples
	A3	PMMA with 2.5 wt% SiO ₂	97.5/2.5	10 Samples
	A4	PMMA with 5 wt% SiO ₂	95/5	10 Samples
	A5	PMMA with 7.5 wt% SiO ₂	92.5/7.5	10 Samples
	A6	PMMA with 10 wt% SiO ₂	90/10	10 Samples
B (Bending strength test) (ISO-178)	B1	Commercial Triplex Hot base composite (For the sake of comparison)	-	10 Samples
	B2	Neat PMMA (control group)	100/0	10 Samples
	B3	PMMA with 2.5 wt% SiO ₂	97.5/2.5	10 Samples
	B4	PMMA with 5 wt% SiO ₂	95/5	10 Samples
	B5	PMMA with 7.5 wt% SiO ₂	92.5/7.5	10 Samples
	B6	PMMA with 10 wt% SiO ₂	90/10	10 Samples
C (Tensile strength test) (ISO-527)	C1	Commercial Triplex Hot base composite (For the sake of comparison)	-	10 Samples
	C2	Neat PMMA (control group)	100/0	10 Samples
	C3	PMMA with 2.5 wt% SiO ₂	97.5/2.5	10 Samples
	C4	PMMA with 5 wt% SiO ₂	95/5	10 Samples
	C5	PMMA with 7.5 wt% SiO ₂	92.5/7.5	10 Samples
	C6	PMMA with 10 wt% SiO ₂	90/10	10 Samples

**Figure 2.** Photograph of the prepared samples for mechanical properties evaluation, including bending (A), tensile (B), and impact (C) analysis (according to ISO-527, ISO-178, and ISO-180, respectively)

3. Results and Discussion

3.1. Morphology Characteristic of Filler Samples

Figure 3 illustrates the surface morphology of the commercial Triplex Hot powder and the synthesized silica aerogel. In the case of commercial triplex hot filler, the FE-SEM micrograph (Figure 3, A-1~A3)

confirmed that the commercial filler is comprised of non-porous filler particles with a micrometric size spherical shape and micron-size fibers with a smooth surface. On the contrary, the synthesized silica aerogel (Figure 3, B1~B3) consisted of a 3D nano-sized interconnected silica network with a nanosized pore characteristic.

BET and FTIR Analysis

The results of texture analysis, as well as surface chemistry analysis of the synthesized silica aerogel and Triplex Hot base fillers, are presented in Figure 4. The adsorption isotherm (from BET analysis) of Triplex Hot base filler depicts a relatively horizontal plateau with a constant slope in the hole process (i. e., 0.99) accompanied by a rapid soar at high relative pressure. The sorption isotherm shows a little nitrogen adsorption at low relative pressure, which is characteristic of materials with low micro-pore properties. The desorption isotherm is also consistent with the sorption isotherm, which is due to the presence of pores with end-capped characteristics [25, 26]. From physisorption analysis, the Triples Hot base filler demonstrates a specific surface area of 7 m². g⁻¹ and a maximum pore size distribution peaked at 1.7 nm. On the contrary, the adsorption-desorption isotherm of the synthesized silica aerogel (see Fig. 4, B-1) behaves like a type IV, IUPAC classification isotherm with the hysteresis loop type of H-3, which

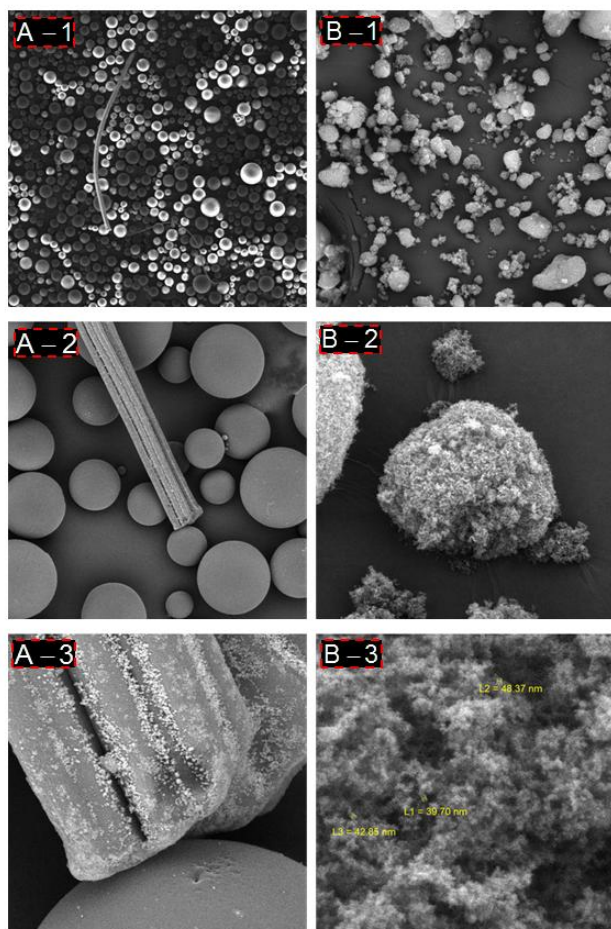


Figure 3. FE-SEM analysis of the commercial Triplex Hot resin base filler (A-1~A3) as well as the as-prepared silica aerogel (B-1~B-3). The EDAX analysis from the Triplex Hot resin and silica aerogel fillers is presented in Figs. A-4 and B-4, respectively

is characteristic of the mesoporous structure. The rapid rise at high relative pressure (in the sorption isotherm) with the out-of-level characteristic results from the N_2 capillary condensation in mesopores of the silica aerogel [27-29]. From the N_2 physisorption analysis, the synthesized silica aerogel shows a specific surface area of $427 \text{ m}^2 \cdot \text{g}^{-1}$ with the main pore size distribution peaked at 12.4 nm.

Figure 4, A-2 represents the recorded FTIR spectrum from the Triplex Hot base filler. The observed vibration bands at wavenumbers of 2950 cm^{-1} and 3009 cm^{-1} , as well as 1459 cm^{-1} , correspond to the stretching and bending modes of the C-H group, respectively. However, the observed bands at 3533 cm^{-1} and 3625 cm^{-1} are related to N-H stretching vibration, whereas the observed peaks at 1639 cm^{-1} , 1459 cm^{-1} , 1430 cm^{-1} , 978 cm^{-1} , 838 cm^{-1} , and 486 cm^{-1} are the adsorption band frequencies characteristic of TiO_2 [30-33]. Figure 4, B-2 illustrates the surface

chemistry properties of the synthesized silica aerogel. As revealed in the FTIR analysis, the adsorption bands at wavenumbers of 3437 cm^{-1} and 1650 cm^{-1} are corresponding to the vibrational mode of the hydroxyl group (O-H), as a result of the presence of unreacted O-H on the SiO_2 surface (i. e., Si-OH) or the adsorbed water in form of humidity. The adsorption bands at 2920 cm^{-1} and 1409 cm^{-1} are due to the stretching and bending vibration modes of the C-H group, respectively, which is introduced during the chemical surface modification process. The observed peaks at 1124 cm^{-1} (intensive peak), 817 cm^{-1} , and 490 cm^{-1} are related to the asymmetric, symmetric, and bending modes of silane chemical bonds (i. e., Si-O-Si), respectively. The observed peaks at wave numbers 2920 cm^{-1} and 1422 cm^{-1} are also due to the presence of the Si-C chemical group [34-36].

3.2. Mechanical Characteristic Analysis

Figure 5 illustrates the mechanical properties (i.e., tensile, impact, and bending strength) of the fabricated PMMA control group and the SiO_2 -PMMA nanocomposites (as a function of SiO_2 filler content). From the experimental results, it was found that the tensile strength of the neat PMMA and Triplex Hot base composite were equal to 12.1 and 14.6 MPa, respectively, as defined in Figure 5 by the red rectangular scatter. In the case of SiO_2 nanocomposites, the tensile strength of the prepared samples increased significantly (from 12.7 to 16.3 MPa) when SiO_2 filler content increased from 0 to 7.5 wt%. On the contrary, the tensile strength of the prepared composites decreases by about 14% (from 16.3 to 14.2 MPa) by a further increase in SiO_2 content from 7.5 to 10 wt%. Similar results were observed for impact and bending strength of the fabricated composites in the same range of silica aerogel filler content (i.e., from 0 to 10 wt%). When the loading content of SiO_2 varied from 0 to 7.5 wt%, the impact strength of the fabricated composites improved significantly from 15.7 to 22.9 MPa. On the contrary, when SiO_2 content increased from 7.5 to 10 wt%, the impact strength of the composites decreased abruptly (about 20%). However, the impact strength of the Triplex Hot base composite (control group) was found to be $19.8 \text{ KJ} \cdot \text{m}^{-2}$, as presented in Figure 5 by the red rectangular scatter. In the case of bending strength, the bending strength of composites is enhanced from 23.7

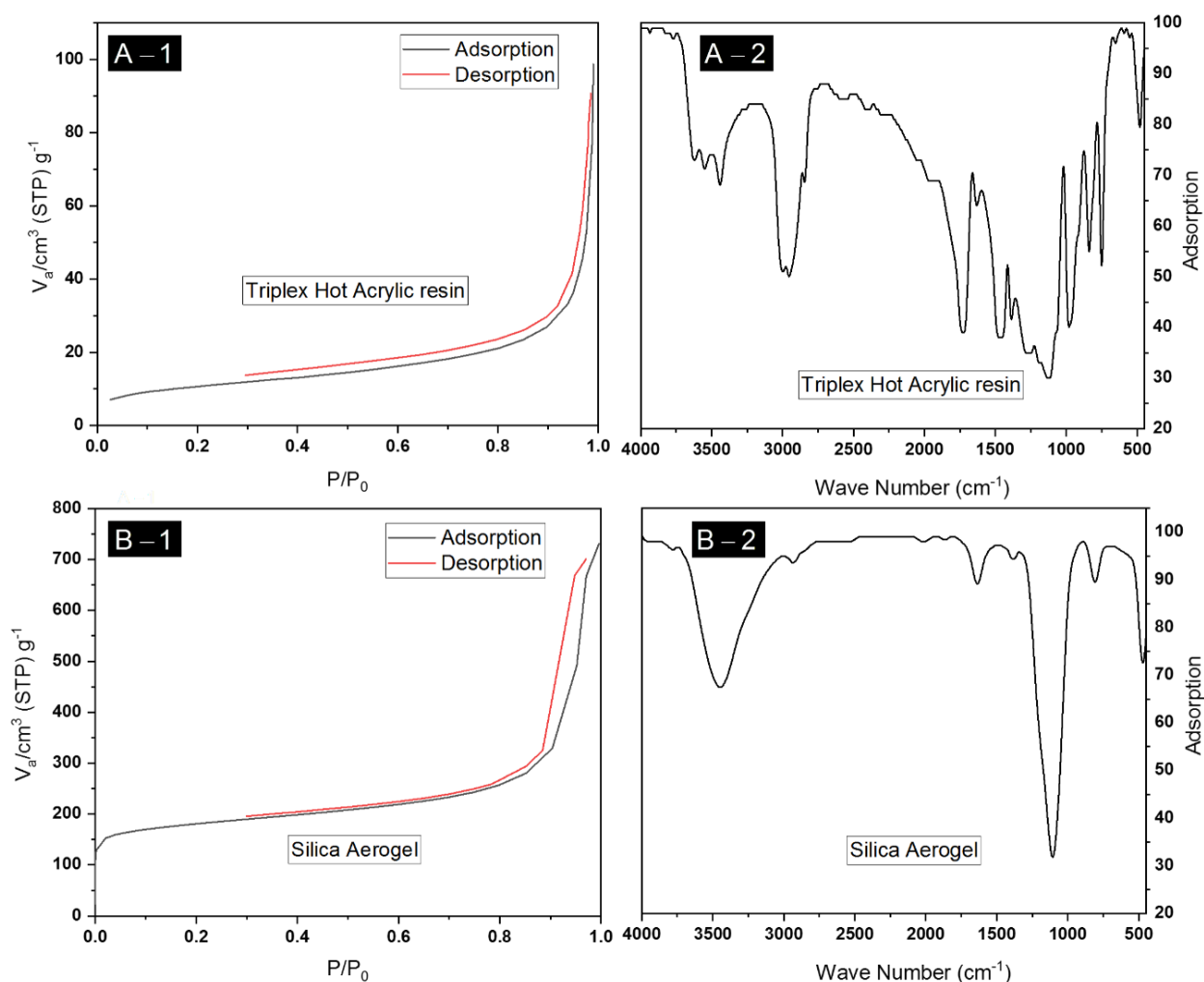


Figure 4. The obtained physisorption analysis from the commercial base Triplex Hot (A-1) and silica aerogel (B-1) fillers, as well as surface chemistry (FTIR) analysis of the Triplex Hot (A-2) and silica aerogel (B-2)

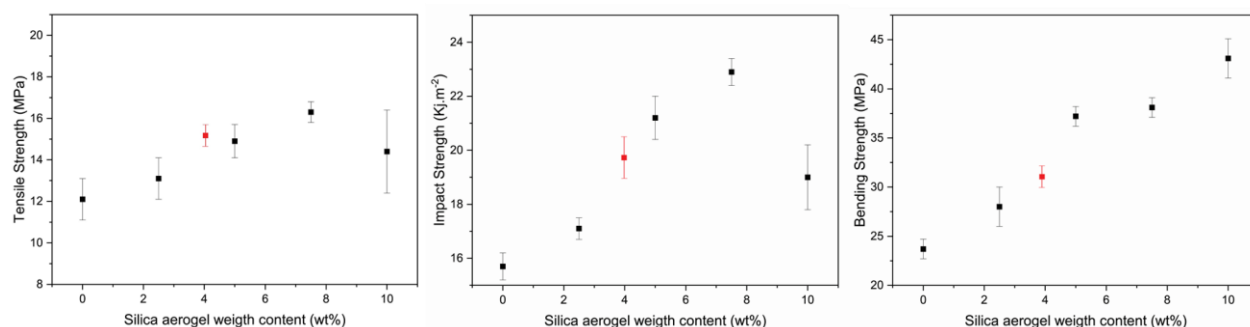


Figure 5. The mechanical properties of the fabricated PMMA dental base composites. (The red symbol is ascribed to the triplex hot base composite)

to 43.1 MPa when the silica aerogel weight content increases from 0 to 10 wt%. The bending strength of the Triplex Hot base composite was also found to be 30.3 MPa.

The experimental results indicate that compared with Triplex hot base composite containing TiO_2 filler

weight content of 10 wt%, incorporation of low weight content of nanoporous silica aerogel (i.e., 7.5 wt%) can elevate the mechanical properties of the MMA resin effectively. At optimum weight content of SiO_2 , the mechanical properties of the SiO_2/PMMA nanocomposites in terms of impact, tensile, and bending strength are enhanced by about 18.7%, 8%,

and 25%, respectively. The reason for such a significant difference in mechanical properties of the reinforced PMMA resin with the synthesized silica aerogel and commercial Triplex Hot fillers could be explained by the difference in interfacial bonding between polymer matrix/ fillers, indicating that chemical surface modification, as well as porous characteristic of the silica aerogel, can augment the interfacial bonding and consequently the mechanical properties of the final composites. It is well known that both specific surface area and interfacial bonding between polymer matrix and filler are two top critical key factors ameliorating the mechanical properties of composites. Hence, in the present study, to improve the interfacial bonding and miscibility between SiO_2 fillers and PMMA matrix, the chemical surface modification of the as-prepared nano-porous silica wet gels with silane chemical functions has been performed. On the other hand, the preparation of hydrophobic silica aerogel resulted in high adhesion between filler and matrix, and consequently, the formation of SiO_2 /PMMA nanocomposite with homogenized dispersion of SiO_2 particles, which can hinder crack initiation and crack deflection mechanisms. The previous studies on the topic also prove that the utilization of nano-sized reinforcements has positively influenced the flexural properties of PMMA-based overdenture composites with the optimum concentration below 10 wt%. As shown in Figure 5, the presence of porous silica also improves the bending strength of the composites, and under the present experimental conditions, it is enhanced significantly from 23.7 to 43.1 MPa when the silica aerogel weight content increases from 0 to 10 wt%. However, the bending strength of the Triplex Hot base composite was calculated to be 30.3 MPa, as defined in Figure 5 by the red rectangular scatter.

The pore characteristic of the filler is also a crucial variable influencing the mechanical properties of the final composites. In the case of structural characteristics of the reinforcement, it was concluded that, compared with neat PMMA and Triplex hot base composite, incorporation of nanoporous silica aerogel can elevate the mechanical properties of the overdenture base acrylic resin. The cage-like structure of the silica aerogel can confine the MMA monomer during the mixing, resulting in proceeding MMA polymerization proceeding from inside to the outside of the nanoporous silica particles and the formation of

a uniform structure with strong interfacial interactions that lead to improved stress propagation and greater stiffness of the final SiO_2 /PMMA nanocomposites. It can be concluded from the literature that there is a lack of research about the effect of porous silica on the mechanical properties of acrylic base composites. Zang *et al* [37] investigated the structural characteristics of the prepared PMMA/meso-cellular foam silica nanocomposites through batch emulsion polymerization. The TEM analysis showed that during polymerization, the MMA monomer can penetrate through silica open pores and fill them, resulting in the formation of a uniform structure with enhanced thermal and mechanical properties (10 wt% loading), including tensile strength (15%) and Young's modulus (19%).

To investigate the relationship between microstructural characteristics and mechanical properties of the as-prepared composites, the FE-SEM analysis was conducted from the surface of the fractured samples (from tensile analysis), and the results are presented in Figure 6. The SEM analysis indicates that the polymerized PMMA resin (see Figure 6A) exhibits the brittle type surface fracture with a river-like stress propagation, which is a result of the stress propagation across the PMMA resin. On the contrary, the prepared commercial Triplex Hot-based composite (see Figure 6B) shows surface fracture with debonding characteristics, which is due to the low interfacial bonding between TiO_2 fibers and MMA resin. This phenomenon is responsible for the weak mechanical properties of the prepared Triplex Hot-based composite during the tension processes. The surface fracture of the silica aerogel/PMMA nanocomposites (Figures. 6C~ E) reveals that the prepared SiO_2 /PMMA nanocomposites containing 2.5-7.5 wt% of SiO_2 presented a condensed texture structure due to the homogenous dispersion and well-embedded nano-porous silica aerogel in MMA matrix. As presented in Figure 6C, the fractured surface of PMMA composite containing 2.5 wt% of SiO_2 displays a large cleavage plane with a uniform facet along the tension direction, which is a typical form of brittle fracture. Although the fractured surface of SiO_2 /PMMA composite containing 2.5 wt% is rougher than neat PMMA, the prepared sample demonstrates a brittle failure. On the contrary, composites containing 5 and 7.5 wt% of SiO_2 show a ductile failure with plastic deformation of the polymer matrix. The ductile

fracture characteristic of the prepared nanocomposite is due to the high surface compatibility between the synthesized silica aerogel and MMA, which are characteristic of composites with higher strength and modulus at optimum filler concentration. By a further increase in SiO_2 content from 7.5 to 10 wt%, the fracture morphology of the prepared composites changes significantly (Figure 6F). From the experimental results, it can be concluded that by such an increase in SiO_2 weight content beyond a critical value (i. e., 7.5 wt%) the strong attractive force between SiO_2 particles leads to a decrease in the filler dispersion and formation of a large spot of SiO_2 agglomeration. On the other hand, the SEM analysis from the fractured surface of the composites containing 10 wt% of SiO_2 maintains that the fracture behavior of the prepared composites is ductile, accompanied by evidence of filler agglomeration appearing as white spots.

Besides the effective influence of nanoporous silica aerogel on the mechanical properties of the prepared nanocomposites, interestingly, the mechanical

characteristic of the as-prepared SiO_2 -PMMA composites also decreases at high loading levels of silica aerogel (i.e., generally higher than 7.5 wt%). Such behavior in the mechanical properties of the as-prepared SiO_2 -PMMA composites may reflect the changes in bonding characteristics between silica aerogel and polymer matrix due to the high agglomeration level of SiO_2 particles. A high concentration of reinforcement filler leads to an increase in filler-filler interactions, which causes the formation of filler agglomeration, acting as a point of stress concentration. This phenomenon leads to non-uniform stress distribution and reduces the mechanical properties (i.e., fracture toughness) of the prepared SiO_2 /PMMA nanocomposites. On the other hand, the formation of voids and clustering of the fillers cause stress concentration and crack propagation by crossing the loaded stress across the filler cluster, resulting in the reduction of the mechanical properties (such as tensile, impact, and bending strength) of the prepared composites.

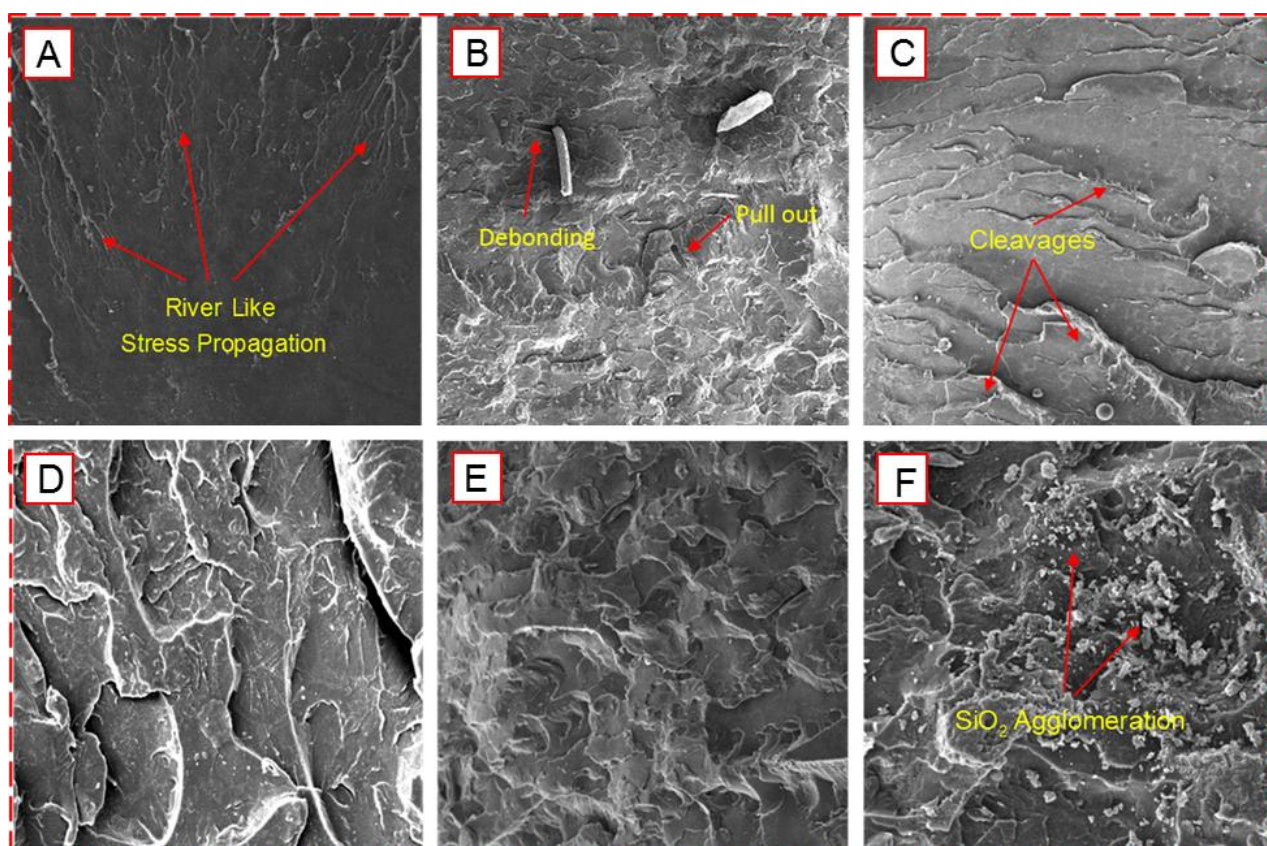


Figure 6. The FE-SEM analysis from the fractured surface of the as-prepared composites. Neat PMMA (A), commercial Triplex Hot composite (B), SiO_2 /PMMA composites containing 2.5, 5, 7, and 10 wt% of SiO_2 (C, D, E, and F, respectively). It should be noted that the surface fracture analysis was performed on samples which were subjected to tensile analysis

Based on the available research about reinforcement of PMMA-based denture materials, it is necessary to compare the performance of the

synthesized aerogel with that in other research. A summary of available research is provided in Table 2. In total, the literature focused on using nano-silica

Table 2. Comparison of the performance of organic solvent removal from acidic electrolytes using different methods

Proposed method	Key process	Highlights	Ref.
Incorporation of nanoporous silica aerogel as composite reinforcement	The maximum mechanical properties of SiO ₂ -PMMA composites were reached in composites containing 7.5 wt% silica aerogel.	At the optimum concentration, the mechanical properties of the prepared composites, including tensile, bending, and impact properties, reached 16.3 MPa, 38.1 MPa, and 22.9 KJ. m ⁻² , respectively.	Present study
hybrid copolymers of methyl methacrylate and methacryloyl grafted nanosilica	Enhancement of fracture properties in PMMA-nanosilica composite materials by incorporating interface modification techniques, specifically through the employment of multilayered structures featuring thin soft poly(ether-ester) (PEA) or hard poly(methyl methacrylate) (PMMA) interlayers.	Thin PEA layers lead to toughening through crack smoothing, but the Young's modulus decreases, while thicker PMMA layers produce	[38]
Effect of adding different quantities of nanosilica to autopolymerized poly(methyl methacrylate) on its mechanical properties.	The autopolymerized poly(methyl methacrylate) (PMMA) denture reline resin was modified by incorporating treated hydrophobic fumed silica (7 nm) with methyl methacrylate liquid component at varying loadings (0.05%, 0.2%, and 1.5% nanosilica).	The addition of 7 nm 0.05% SiO ₂ is the most effective in increasing flexural modulus and strength of autopolymerized poly(methyl methacrylate) based on nanosilica.	[39]
supercritical processing of nanosilica sol in composites with improved mechanical properties compared to neat PMMA.	Nanosilica/PMMA composites were investigated for their mechanical properties using both conventional and supercritical coating methods.	The resulting nanosilica/PMMA composite containing nanoparticles obtained by supercritical processing of the nanosilica sol showed an increase in hardness by 44.6% and elastic modulus by 25.7% relative to neat PMMA.	[40]
the combination of graphene oxide (GO) and mesoporous micro-silica particles with varying pore sizes was used as fillers in PMMA matrices	Offers the possibility of further enhancement of thermal and mechanical properties of polymer-based composites by incorporating more than one filler with diverse properties.	-Thermal stability (the temperature at 10% and 60% weight loss), Td10 and Td60 increased by 46.5 °C and 32.3 °C, respectively.	[41]
Effect of fumed silica weight content on mechanical and structural properties of PMMA denture base material.	The effect of adding fumed silica at different contents (0.5%, 1%, and 2%) to PMMA mechanical properties was investigated.	-Tensile strength increased remarkably. fumed silica specimens with a concentration of 1% by weight (wt%) exhibited the highest energy storage capacity (3.24 GPa at 30 °C) and glass transition temperature, thereby indicating that the maximum saturation limit of fumed silica in poly(methyl methacrylate) (PMMA) denture base material was achieved at this concentration. Conversely, samples containing 2% fumed silica exhibited increased brittleness, an effect attributed to the surface accumulation of fumed silica particles.	[42]
Effect of multicomponent additives on mechanical properties of PMMA based prosthetic complete denture materials	Effect of adding nanohydroxyapatite (nHA) and micro-zirconia (ZrO ₂) particles, as well as E-glass and Kevlar fibers, on the mechanical properties of poly methyl methacrylate (PMMA) cold cure resin used in prosthetic dentures.	The study concludes that the addition of nanohydroxyapatite (nHA) and micro-zirconia (ZrO ₂) particles, as well as E-glass and Kevlar fibers, improves the mechanical properties of poly methyl methacrylate (PMMA) cold cure resin used in prosthetic dentures	[43]

under different processing conditions to improve the mechanical properties of the resulting nanocomposites.

4. Conclusion

Within the consideration of the present study's limitations, the following conclusions can be inferred. The incorporation of silica aerogel enhances the tensile, bending, and impact fracture of the heat-polymerized PMMA-based overdenture resin. The experimental results show that in all samples except at SiO₂ filler loading of 2.5 wt%, the tensile strength of the as-prepared nano-composites is higher than that of commercial acrylic overdenture base materials. The maximum mechanical properties of SiO₂-PMMA composites were reached in composites containing 7.5 wt% silica aerogel. At the optimum concentration, the mechanical properties of the prepared composites, including tensile, bending, and impact properties, reached 16.3 MPa, 38.1 MPa, and 22.9 KJ. m⁻², respectively. The results revealed that the utilization of 3D nano-porous silica aerogel can improve the mechanical properties of the fabricated composites due to the increase in tension propagation pathways along with the 3D directions. Hence, increasing the propagation pathway of the induced forces can effectively dissipate the kinetic energy of the loaded forces, improving the mechanical properties of the reinforced PMMA resin by using nanoporous silica aerogel.

References

- 1- Ahmed Nabhan, Mohamed Taha, and Nouby M Ghazaly, "Filler loading effect of Al₂O₃/TiO₂ nanoparticles on physical and mechanical characteristics of dental base composite (PMMA)." *Polymer Testing*, Vol. 117p. 107848, (2023).
- 2- Harini Sosiati, Arif Muhammad Rizky, Aldi Lukman Maulana Latief, Rahmad Kuncoro Adi, and Sinin Hamdan, "The mechanical and physical properties of microcrystalline cellulose (MCC)/sisal/PMMA hybrid composites for dental applications." *Materials Research Express*, Vol. 10 (No. 3), p. 035301, (2023).
- 3- Ilaria Roato *et al.*, "mechanical and biological characterization of PMMA/Al₂O₃ composites for dental implant abutments." *Polymers*, Vol. 15 (No. 15), p. 3186, (2023).
- 4- Bo Cao, Peng Wu, Wenxiang Zhang, Shumei Liu, and Jianqing Zhao, "The Fabrication of High-Hardness and Transparent PMMA-Based Composites by an Interface Engineering Strategy." *Molecules*, Vol. 28 (No. 1), p. 304, (2022).
- 5- Moe Kubota *et al.*, "Setting behaviour, mechanical properties and heat generation under alternate current magnetic fields of Fe₃O₄/TiO₂/PMMA composite bone cement." *Medical Devices & Sensors*, Vol. 3 (No. 6), p. e10114, (2020).
- 6- Rajan Choudhary, Senthil Kumar Venkatraman, Inna Bulygina, Fedor Senatov, Sergey Kaloshkin, and Sasikumar Swamiappan, "Designing of porous PMMA/diopside bone cement for non-load bearing applications." *Journal of Asian Ceramic Societies*, Vol. 8 (No. 3), pp. 862–72, (2020).
- 7- Ban Ali Sabri, Meenaloshini Satgunam, NM Abreeza, and Abdulrahman N. Abed, "A review on enhancements of PMMA denture base material with different nano-fillers." *Cogent Engineering*, Vol. 8 (No. 1), p. 1875968, (2021).
- 8- Mohamed Ashour Ahmed, M El-Shennawy, Yousef M Althomali, and Adel A Omar, "Effect of titanium dioxide nano particles incorporation on mechanical and physical properties on two different types of acrylic resin denture base." *World Journal of Nano Science and Engineering*, Vol. 6 (No. 3), pp. 111–19, (2016).
- 9- Touraj Nejatian, Neil Nathwani, Louise Taylor, and Farshid Sefat, "Denture base composites: Effect of surface modified nano-and micro-particulates on mechanical properties of polymethyl methacrylate." *Materials*, Vol. 13 (No. 2), p. 307, (2020).
- 10- Pornpot Jiangkongkho, Mansuang Arksornnukit, and Hidekazu Takahashi, "The synthesis, modification, and application of nanosilica in polymethyl methacrylate denture base." *Dental materials journal*, Vol. 37 (No. 4), pp. 582–91, (2018).
- 11- Maneerat Songpanit *et al.*, "Self-cleaning SiO₂/TiO₂/PMMA nanocomposite films fabricated by spin coating technique: Effect of different spin speed and film layers." *Journal of Materials Science and Applied Energy*, Vol. 12 (No. 3), pp. 252043–43, (2023).
- 12- Manal A Awad, Awatif A Hendi, Khalid MO Ortashi, Amnah B Alanazi, Batool A ALZahrani, and Dina A Soliman, "Greener Synthesis, Characterization, and Antimicrobial Effects of Helba Silver Nanoparticle-PMMA Nanocomposite." *International Journal of Polymer Science*, Vol. 2019 (No. 1), p. 4379507, (2019).
- 13- Sonali B Jadhavar, Rajaram S Sutar, Sanjay S Latthe, and RS Vhatkar, "Preparation of superhydrophobic coating using silica-pmma nanocomposite." in *Macromolecular Symposia*, (2020), Vol. 393 (No. 1): Wiley Online Library, p. 2000161.

- 14- Mi Tian *et al.*, "Nanoporous polymer-based composites for enhanced hydrogen storage." *Adsorption*, Vol. 25pp. 889–901, (2019).
- 15- Pinar Cay-Durgun and Mary Laura Lind, "Nanoporous materials in polymeric membranes for desalination." *Current opinion in chemical engineering*, Vol. 20pp. 19–27, (2018).
- 16- Saeed Salimian, Ali Zadhoush, and Zahra Talebi, "Interpenetrating organic–inorganic network: A short review on aerogel as a nanoporous filler in epoxy nanocomposite." *Material Design & Processing Communications*, Vol. 1 (No. 6), p. e107, (2019).
- 17- Jinlong Tan *et al.*, "Influence of the Addition of Nanoporous Graphite/Paraffin Additive on the Wear Properties of Phenol-Formaldehyde Resin Composites." *Journal of Macromolecular Science, Part B*, Vol. 58 (No. 1), pp. 88–98, (2019).
- 18- Steven J McNeil and Honey Gupta, "Emerging applications of aerogels in textiles." *Polymer Testing*, Vol. 106p. 107426, (2022).
- 19- Ying Du and Hee-Eun Kim, "Research trends of the application of aerogel materials in clothing." *Fashion and Textiles*, Vol. 9 (No. 1), p. 23, (2022).
- 20- HPS Abdul Khalil *et al.*, "Biopolymers based aerogels: A review on revolutionary solutions for smart therapeutics delivery." *Progress in Materials Science*, Vol. 131p. 101014, (2023).
- 21- Mohammad Oves, Mohd Ahmar Rauf, Mohinuddin Khan Warsi, Fohad Mabood Husain, Mohammad Omaish Ansari, and Iqbal MI Ismail, "Aerogels as microbial disinfectant." in *Advances in Aerogel Composites for Environmental Remediation: Elsevier*, (2021), pp. 201–15.
- 22- Wenxian Lian, Jie Zhang, Weixin Liu, Kun Liu, and Shaokun Tang, "Monolithic chitosan-silica composite aerogel with comprehensive performances prepared by SBG-FD method." *Ceramics International*, Vol. 49 (No. 13), pp. 21947–56, (2023).
- 23- Hajar Maleki and Nicola Huesing, "Silica-silk fibroin hybrid (bio) aerogels: two-step versus one-step hybridization." *Journal of Sol-Gel Science and Technology*, Vol. 98pp. 430–38, (2021).
- 24- Andrea Kuttar *et al.*, "Preparation and application of highly porous aerogel-based bioactive materials in dentistry." *Frontiers of Materials Science*, Vol. 8pp. 46–52, (2014).
- 25- Sapna B Jadhav, Arwa Makki, Dina Hajjar, and Pradip B Sarawade, "Synthesis of light weight recron fiber-reinforced sodium silicate based silica aerogel blankets at an ambient pressure for thermal protection." *Journal of Porous Materials*, Vol. 29 (No. 4), pp. 957–69, (2022).
- 26- Ha-Yoon Nah *et al.*, "Silylation of sodium silicate-based silica aerogel using trimethylethoxysilane as alternative surface modification agent." *Journal of Sol-Gel Science and Technology*, Vol. 87pp. 319–30, (2018).
- 27- Ozgur Kaya Cakmak, Khalil T Hassan, Jiabin Wang, Xiao Han, and Lidija Šiller, "Synthesis of sodium silicate-based silica aerogels with graphene oxide by ambient pressure drying." *Journal of Porous Materials*, Vol. 28 (No. 5), pp. 1545–52, (2021).
- 28- Bartosz Babiarczuk *et al.*, "Mechanical properties of silica aerogels controlled by synthesis parameters." *Journal of Non-Crystalline Solids*, Vol. 606p. 122171, (2023).
- 29- Seyed Saeed Mirzaee, Esmaeil Salahi, and Ali Khanlarkhani, "Modelling and optimisation of sodium silicate based silica aerogel synthesis using response surface methodology." *Micro & Nano Letters*, Vol. 13 (No. 6), pp. 853–56, (2018).
- 30- Qais M Al-Bataineh, Ahmad A Ahmad, AM Alsaad, and Ahmad D Telfah, "Optical characterizations of PMMA/metal oxide nanoparticles thin films: bandgap engineering using a novel derived model." *Heliyon*, Vol. 7 (No. 1), (2021).
- 31- Pablo Aguilar-Rodríguez, Sandra Zetina, Adrián Mejía-González, and Nuria Esturau-Escofet, "Microanalytical Characterization of an Innovative Modern Mural Painting Technique by SEM-EDS, NMR and Micro-ATR-FTIR among Others." *Molecules*, Vol. 28 (No. 2), p. 564, (2023).
- 32- Francisco Javier GAYTÁN-LARA, ZÁRRAGA-NÚÑEZ Ramón, and Rosario GALINDO-GONZÁLEZ, "Synthesis and incorporation of ZnO/TiO₂ in PMMA to study its thermal properties." *Volume 7, Issue 12–January–June–2020*, p. 17, (2020).
- 33- Leila Mohammadi Amirabad, Mohammadreza Tahriri, Payam Zarrintaj, Reza Ghaffari, and Lobat Tayebi, "Preparation and characterization of TiO₂-coated polymerization of methyl methacrylate (PMMA) for biomedical applications: In vitro study." *Asia-Pacific Journal of Chemical Engineering*, Vol. 17 (No. 3), p. e2761, (2022).
- 34- Fatoş Koç, Selay Sert Çok, Nilay Gizli, F Koc, S Sert Cok, and N Gizli, "Tuning the properties of silica aerogels through pH controlled sol-gel processes." *Research on Engineering Structures and Materials*, Vol. 6 (No. 3), pp. 257–69, (2020).
- 35- Debabrata Panda and Krupal M Gangawane, "Superhydrophobic hybrid silica-cellulose aerogel for enhanced thermal, acoustic, and oil absorption characteristics." *Journal of Materials Science*, Vol. 57 (No. 28), pp. 13385–402, (2022).
- 36- Gulcihan Guzel Kaya, Elif Yilmaz, and Huseyin Deveci, "Synthesis of sustainable silica xerogels/aerogels using inexpensive steel slag and bean pod ash: A comparison study." *Advanced Powder Technology*, Vol. 31 (No. 3), pp. 926–36, (2020).

- 37- Fa-Ai Zhang, Dong-Keun Lee, and Thomas J Pinnavaia, "PMMA–mesocellular foam silica nanocomposites prepared through batch emulsion polymerization and compression molding." *Polymer*, Vol. 50 (No. 20), pp. 4768–74, (2009).
- 38- Stéphane Cros, Alain Burr, André Dubault, and Jean Louis Halary, "Upgrading of the fracture properties of multi-layered PMMA-nanosilica materials by interface modification." *Composite Interfaces*, Vol. 14 (No. 2), pp. 85–98, (2007).
- 39- Sebastian Baloš, Branka Pilić, Djordje Petrović, Branislava Petronijević, and Ivan Šarčev, "Flexural strength and modulus of autopolimerized poly (methyl methacrylate) with nanosilica." *Vojnosanitetski pregled*, Vol. 75 (No. 6), (2018).
- 40- D Stojanovic, A Orlovic, S Markovic, V Radmilovic, Petar S Uskokovic, and R Aleksic, "Nanosilica/PMMA composites obtained by the modification of silica nanoparticles in a supercritical carbon dioxide–ethanol mixture." *Journal of Materials Science*, Vol. 44 (No. 23), pp. 6223–32, (2009).
- 41- Hafsa Naznin, Abul K Mallik, Khandker S Hossain, MD Shahruzzaman, Papia Haque, and Mohammed Mizanur Rahman, "Enhancement of thermal and mechanical properties of PMMA composites by incorporating mesoporous micro-silica and GO." *Results in Materials*, Vol. 11p. 100203, (2021).
- 42- Hakki Cenker Kucukesmen and Mehmet Fahri Sarac, "Preparation and characterization of fumed silica added PMMA denture base materials." *International Journal of Polymer Analysis and Characterization*, pp. 1–10, (2024).
- 43- Sihama I Salih, Jawad K Oleiwi, and Qahtan A Hamad, "Studying the tensile properties and morphology test for the self cured PMMA resin of prosthetic complete denture." *The Iraqi Journal For Mechanical And Material Engineering, Special Vol., Part II*, pp. 508–22, (2015).