Addition effect of partially stabilized zirconia ($ZrO_2.Y_2O_3$) filler on some properties of unsaturated polyester resin base matrix composite for In-Vivo applications

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Abstract

Polyester-based materials are established options, concerning the production of bone fixation apparatuses as well as the apparatuses in routine clinical application. The objective of present work is to assess the influence of partially stabilized zirconia (PSZ) particles incorporation using 5.4%wt. of Yittria particles ($ZrO_2.Y_2O_3$) on some mechanical properties and water absorption of unsaturated polyester, as well as to establish which features of such material provide the best outcomes aiming their biomedical implementation. The effect of added ceramic filler of partially stabilized zirconia (PSZ) ($ZrO_2.Y_2O_3$) on the tensile strength, hardness, impact strength, and the water absorption percentage of the unsaturated polyester resin base composite, was studied at the weight fractions of (1, 2, 3, 4, 5, and 6) % wt. and the particle size < 53 µm. Tensile strength and modulus of elasticity reached their peak values at a 2% weight of PSZ. In contrast, impact strength, hardness, and water absorption percentage exhibited their highest values at higher PSZ ratios. The addition of PSZ particles resulted in a decrease in elongation percentage overall.The addition of PSZ particles at a certain amount manifested a positive influence upon the unsaturated polyester improving their utilization in the medical field, particularly if some anatomical areas require higher materials strength, giving long life for the rehabilitation, and providing the potential for improving the clinical performances of the fracture fixation apparatuses.

Keywords: Biocomposites, Unsaturated Biopolyesters matrix composite, Biopolymer composite material, Mechanical Properties.

1. Introduction

The materials interfacing with the biological entities are utilized for creating prosthesis; the medical apparatuses as well as replacing the natural body tissue are widely named biomaterials. The biodegradable polyesters utilization in the orthopedic apparatuses for appropriate fixation for lengthy bone fractures was firstly applied clinically in 1984 in Finland. Also, it was revealed that the precise amalgamation of the fracture that fixed via poly-lacticco glycolic acid (PLGA) was five days quicker than the fracture that fixed via traditional metallic implants (Hanna et al.,2011) (Gritsch et al.,2021).

The focus in the biomedical engineering field has moved since the last decade to the biodegradable polymers, particularly, polyesters. Many polyester-based medical apparatuses are obtainable commercially, and each year, further are presented to the marketplace. The mechanical performance as well as the broad range of biodegradation properties of such polymers class allow for elevated degrees of selectivity for the targeted clinical uses (Ulery et al.,2011).

The fractured bones need stabilization to allow the occurrence of healing. Also, for intricate fractures, and in anatomical areas that aren't conducive to the exterior fixation, the interior fracture fixation plates are needed (Naseem et al., 2021). Polylactic acid (PLA) is a synthetic biopolymer that is used extensively in biomedical applications. PLA is aliphatic, biodegradable polyester utilized in bone fixation uses as it's likely to tailor the crystallinity's rate and degree, and thus the mechanical properties, the degradation behavior, and the treatment temperatures (Maleki et al., 2022). The restricted mechanical properties, the deficiency of bioactive conduct allowing the bone apposition as well as the bonding upon the polyester implant, and the difficulties related to the products of acidic degradation are the main disadvantages of polyester implants. The ceramic materials are biocompatible, high strength, corrosion resistant, and some of them possess an elevated bioactivity level, and for this reason, composite polyester implants having ceramic fillers like zirconia were utilized for improving the whole mechanical properties in the bio-resorbable osteo-fixation apparatuses (Naseem et al., 2021).

Bone extra cellular matrix is composed of living cells embedded within a matrix, which consists of three main components, i.e., inorganic phase Hydroxyapatite, organic phase collagen and water (Kolb and Bussard, 2019) (Al-Kazraji et al., 2010). The material for bone substitution should be characterized by chemical compatibility, mechanical stability, and ease of handling. Biocompatibility of a given material is dependent on the material host or tissue interactions which occur over the anticipated duration that the material is in service (Sohn and Oh, 2019) (Yasmin, 2022).

Trauma, de-generation, and diseases frequently make a surgical overhaul or a substitution essential if a person possesses a joint pain. And, in such method, an impermanent scaffold is required for serving as an adhesive substrate for the implanted cells as well as a physical backing for guiding the new organs formation. Also, the scaffold has to be malleable, mechanically strong, most porous having a big ratio of surface to volume, biodegradable, and biocompatible. Additionally, the bio-composites evolution provides a great capability for improving the efficiency of present tissue replacements that being very often single-phase materials, which dearth this property as a diversification. Due to the likenesses with the bone's chemical composition, polymer/ceramic composites were the initial bio-composites regarded for the orthopedic implant uses. Especially for the polymer/ceramic bio-composites, it's likely to determine a broad range of biological and mechanical properties via adjusting the kind and the ceramic phase spreading into the matrix of polymer. Significantly, the augmented interactions between the host tissue and the bio-composites can be performed via optimizing the polymer/ceramic composites; and for such cause, a broad diversity of bio-composites was manufactured for different biomedical uses at present (Kolb and Bussard, 2019) (Al-Kazraji et al., 2010). In 2011, Hanna et al. prepared a bio-composite material by reinforcing polyurethane with varying ratios of CaO, $CaCO_3$, MgO, and $MgCO_3$ particles. They investigated the effects of these additions on various mechanical and physical properties and found that the most significant improvements were achieved using $MgCO_3$ as a reinforcement. In 2010, Al-Kazraji et al. studied the impact of adding calcined and uncalcined hydroxyapatite (HA) powder to unsaturated polyester for potential use as a biomaterial in joint replacement. Their results indicated that both calcined and uncalcined HA increased tensile strength, modulus of elasticity, compression strength, bending strength, fracture toughness, and hardness, with calcined HA showing greater improvements. However, the addition of HA led to a decrease in elongation and impact strength. The water absorption, a key physical property, increased with higher HA ratios. In 2006, Ramakrishna et al. examined the effect of adding granite powder to unsaturated polyester. Their findings demonstrated that the addition of granite powder enhanced the mechanical strength and water absorption capacity of the composite.

2. Materials and Methods

2.1 Materials

2.1.1 Matrix

Unsaturated polyester is the major constituent of the base polymer composite supplied by Industrial Chemicals & Resins Co., Dammam - Kingdom of Saudi Arabia. **Table 1** explains some properties of the used unsaturated polyester.

Table 1. Some properties of the used unsaturated polyester

Property	**Value**	**Unit**
Viscosity	400-500	Cps
Specific Gravity	1.13	g/cc
Acid Value	23-28	Mg/Koh/gm
Styrene Content	38	% weight
Flash Point	34	Centigrade
Gel Time	15-20	Minutes

Exothermic Peak	150-165	Centigrade

2.1.2 Hardener

The unsaturated polyester is a viscose transparent liquid at room temperature, which solidifies to become a thermoset by using a hardener. Methyl Ethyl Ketone Peroxide (MEKP) is the hardener used in this study, which supplied by Industrial Chemicals & Resins Co., Dammam - Kingdom of Saudi Arabia.

2.1.3 Zirconia

Partially stabilized zirconia ($ZrO_2.Y_2O_3$) of particle size < 53 µm stabilized by using 5.4%wt. of Y_2O_3 was used in this study and supplied by Zirconia Sales- GU 18544- U.K. **Table 2** lists the chemical composition of the partially stabilized zirconia (PSZ) utilized in the present work.

Table 2. The chemical composition of the used partially stabilized zirconia

Oxide	**ZrO_2+HFO_2**	**Y_2O_3**	**SiO_2**	**TiO_2**	**Al_2O_3**	**F_2O_3**	**Na_2O**	**CaO**
% wt	93.8	5.4	0.11	0.12	0.25	0.003	0.05	0.05

2.2 Methods

2.2.1 Preparation of specimens

The ceramic filler (PSZ) amount was determined based on the weight fractions and added at a range of (1 - 6) %wt. The amount of unsaturated polyester was calculated based on the cast volume, with a hardener addition of 2% as a weight fraction. The ceramic filler and the matrix were continuously and slowly stirred at a speed of 25 rpm for 15 min until the mixture is homogenized. The slow mixing was recommended to avoid the formation of bubbles while stirring, then a hardener was gently added to the mixture before the end of mixing. The pouring of prepared mixture was started from one of the mold corners (to minimize the creation of bubbles, which might cause the cast damage), till this mold being filled to a suitable level. This mold is located upon an electrical vibrator for eliminating any remaining captured gases because of the mixing and temperature rise, also to ensure that the mix spreads uniformly inside the mold. This mix was left into the cast mold to harden for a period of 24 hr at the room temperature, to ensure the completion of the polymerization, and achieving the highest coherency. All prepared casts were removed from the mold and then located into a dryer furnace overnight at a temperature of 45°C. Such process is necessary for obtaining the best entanglement and removing the stresses generated during the preparation. Then, all casts were aged for one week to relieve the further remaining stresses (Hanna, 2014).

2.3 Tests

2.3.1 Tensile test

Tensile tests were conducted with Instron 1195 tensile test machine, and the samples tests shown in **Figure 1-a**, were prepared in accordance with the ASTM (D638M-87b) (ASTM D638, 2014) as. The test was done at room temperature, with applying a load of 5 KN and a strain rate of 0.5 mm/min.

2.3.2 Impact test

The impact test was conducted using a Charpy Tension Impact Tester, and the samples tests shown in **Figure 1-b** were prepared by following the ISO (179). The Impact strength was calculated using **Equation 1** (Krausz et al., 2021) (Cilleruelo et al., 2012): -

$$IS = \frac{E_c}{h \times b} \qquad (1)$$

Where: IS represents the Impact strength, h is the sample thickness, and b is the sample width.

2.3.3 Hardness test

It was achieved with the Shore (D) test, and the samples tests shown in **Figure 1-c** prepared in accordance with the ASTM (D-2240) (ASTM D2240, 2005).

2.3.4 Water absorption

Samples of water absorption test shown in **Figure 1-d**, were prepared following the ASTM (D 570-98) (ASTM D570, 2005). Water absorption percentage was calculated using **Equation 2** (Hanna, 2014): -

$$Water\ absorption\% = \frac{w_2 - w_1}{w_1} \times 100 \qquad (2)$$

Where:

w_1: is the mass of the sample before immersion (g).

w_2: is the mass of the sample after immersion (g).

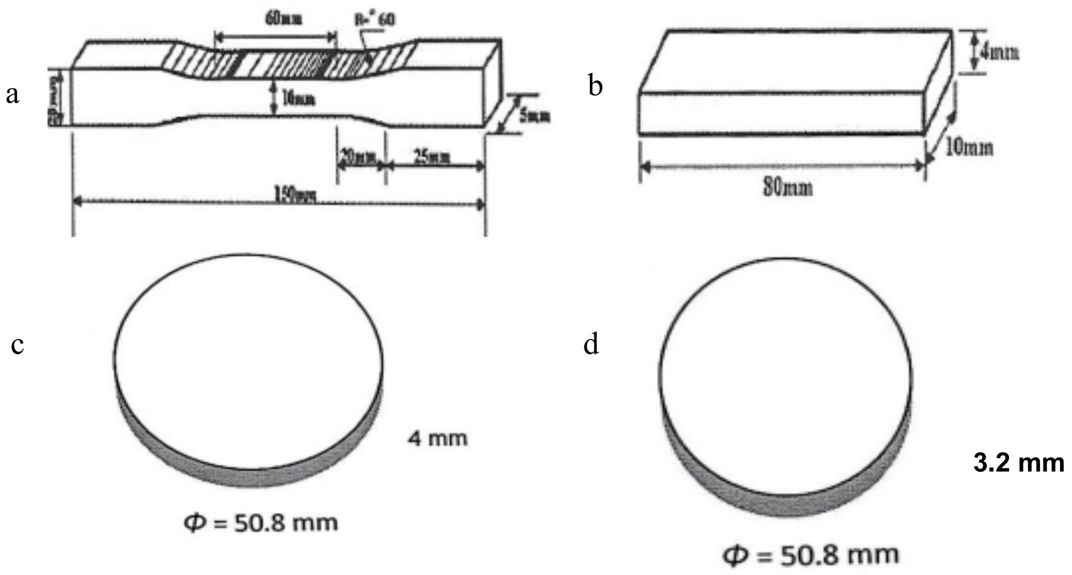

Figure 1. Dimensions of the Specimens used for the prepared biocomposite (Hanna, 2014) and (Krausz et al., 2021). (a-tensile, b-impact, c-hardness, and d-water absorption) tests.

3. Results and Discussions

Tensile strength, elongation%, elastic modulus impact strength, hardness (shore D), and water absorption% results of the prepared unsaturated polyester base composite with the addition of different weight fractions of PSZ (1, 2, 3, 4, 5, and. 6) %wt are depicted in **Table 3** and **Figures 2, 3, 4, 5, 6,** and **7,** respectively.

Table 3. Effect of the PSZ addition on the mechanical properties and water absorption% of

the unsaturated polyester base matrix composite

PSZ % wt.	Tensile Strength MPa	Elongation %	Elastic Modulus GPa	Impact Strength (J/mm^2)	Hardness Shore D	Water Absorption %
0	37.5	7.0	0.8	2.8	83	0.21
1	51	5.25	1.4	2.5	88.3	0.17
2	57	6.75	1.45	2.9	88.3	0.18
3	37	3.25	0.9	1.9	88.7	0.3
4	51	5.0	1.37	1.6	85.7	0.25
5	45	4.0	1.1	3	87	0.25
6	43	4.0	1.0	2.95	89	0.3

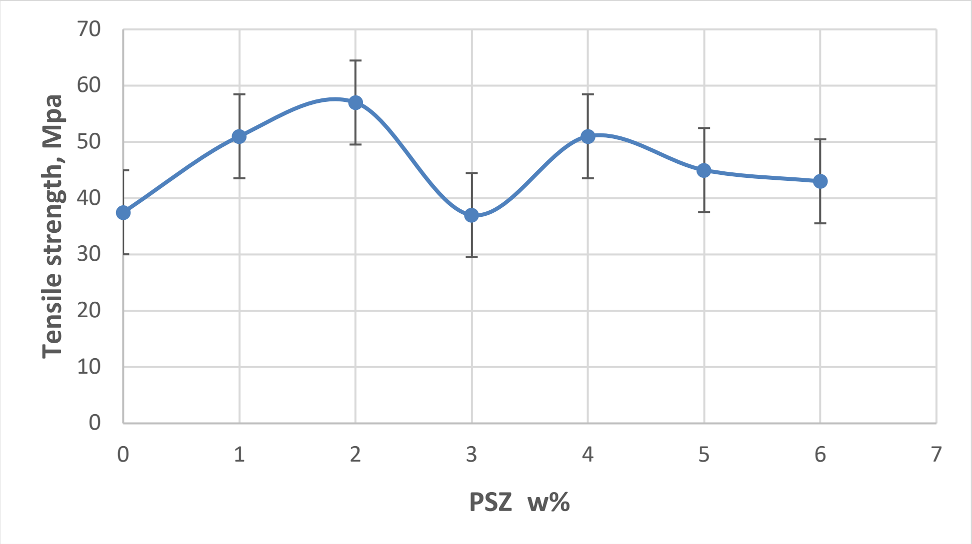

Figure 2. Effect of the PSZ addition upon the tensile strength of the unsaturated polyester base matrix composite.

Table 3 and **Figure 2** explains that the addition of PSZ filler possesses an observable influence upon tensile strength, and the tensile strength reaches its maximum value 57 MPa with the addition of 2%wt. PSZ, compared with the tensile strength of the reference sample which is equal to 37.5 MPa. Also, the results revealed that the tensile strength decreased when adding 3% wt. of PSZ. This decrease in strength may be due to the disorganized distribution and no filler particles wetting with the matrix (Ramakrishna and Rai, 2006). At a higher amount of filler addition, the tensile strength starts decreasing because of the weak interfacial bonding between the PSZ filler particles and the unsaturated polyester resin base matrix composite. Also, the agglomeration of filler particles, and defects such as the porosity might be observed (Yasmin et al., 2006), though the excessive particles that weren't well-dispersed into the polymer base matrix will create stress concentration into the matrix of polymer as well as decreases the tensile strength (Latinwo et al., 2010).

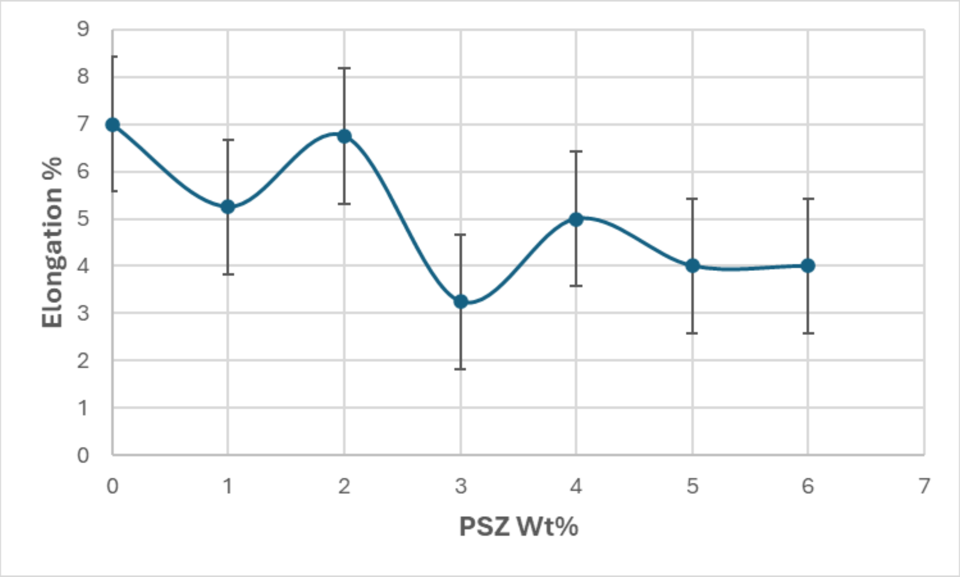

Figure 3. Effect of the PSZ addition upon the elongation % of the unsaturated polyester base matrix composite.

Table 3 and **Figure 3** illustrate the elongation percentage behavior with the addition of different ratios of PSZ. The 2% by weight ratio of PSZ showed the highest elongation percentage in the prepared composite. However, a decrease in elongation percentage was observed at 3% wt., likely due to the agglomeration of PSZ particles as the reinforcement percentage increased (Yasmin et al., 2006).

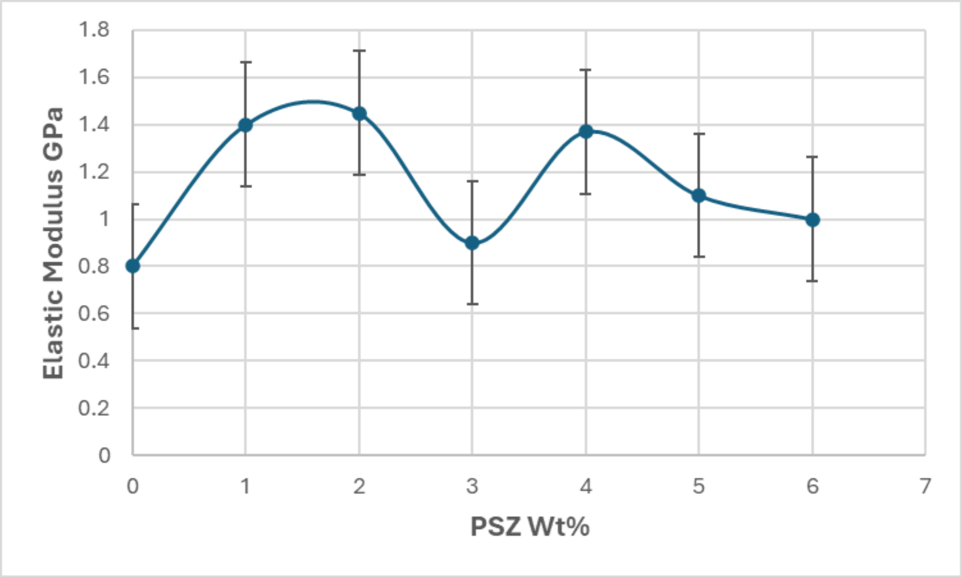

Figure 4. Effect of the PSZ addition upon the elastic modulus of the unsaturated polyester base matrix composite.

Table 3 and **Figure 4** displays clearly that the elastic modulus is directly proportional to the tensile stress reaching its maximum value 1.45 GPa with the addition of 2%wt. of the PSZ.

Table 3 and **Figure 5** manifest the relation between the impact strength and the weight fraction of PSZ that was added to the unsaturated polyester resin base matrix composite in the range of (1- 6) % wt. The maximum impact energy of the prepared composite reaches its maximum value 3.0 J/mm^2 at the addition of 5%wt. of PSZ to the unsaturated polyester resin base composite, comparing with the impact strength of the reference sample 2.8 J/mm^2. The results elucidated that the impact strength reduces with the addition of 3% wt. and 4% wt. of PSZ to the prepared polymer composite. If a composite being exposed to an impact, then a quick crack spread is started throughout the material. And, if this crack spread meets the particles of filler into the packed composites, the particles of filler can absorb the energy as well as halt the crack spread when the filler-matrix interaction being vigorous. In different words, when the interfacial adhesion is deprived, then it cannot withstand the crack spread as efficiently as the polymer only and as a result, it spreads a disastrous crack that lowers the impact strength (Ramakrishna and Rai, 2006) (Shivamurthy and Prabhuswamyc, 2009). This eventually results in a reduction in the composites' impact strength as the filler loading raises.

Also, the filler agglomeration tendency leads to feebler interfacial zones. Additionally, the agglomerates will work as the points of stress concentration or the crack start locations. Thus, a decrease in the impact strength is expected (Ramakrishna and Rai, 2006). The material elasticity decreases owing to the addition of filler as well as the agglomeration will reduce the matrix deformability and in sequence the skin area's ductility, so as the composite have a tendency to develop a feeble structure too. Then, the less ability of matrix to absorb the energy will cause reducing the toughness, which decreases the impact strength (Sreekanth et al., 2009) (Sreekanth et al., 2009) (Bose and Mahanwar, 2004).

Table 3 and **Figure 6** elucidate respectively the relation between the hardness and the weight fraction of the PSZ that was supplemented to the unsaturated polyester resin. Also, the outcomes demonstrated that the hardness rises with raising the weight fraction of the particles of filler as well as attains its maximum value 89.0 with the addition of 6%wt. PSZ compared with the reference sample's hardness 83.

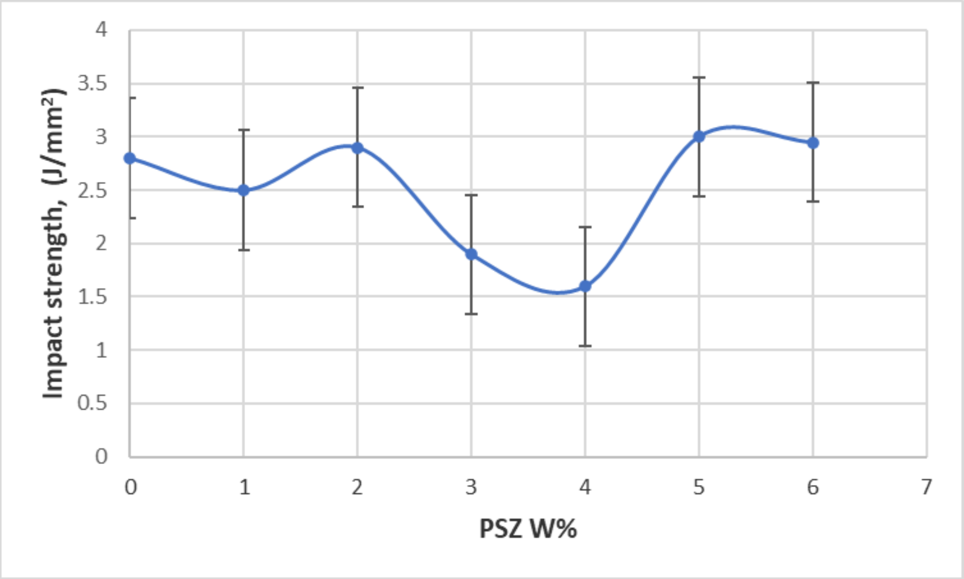

Figure 5. Effect of PSZ addition upon the impact strength of the unsaturated polyester base matrix composite.

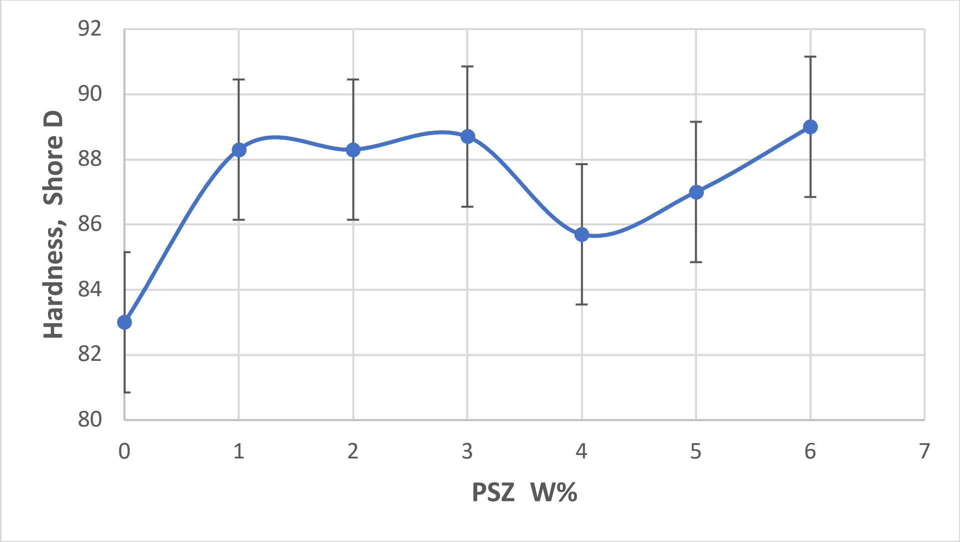

Figure 6. Effect of the PSZ addition upon the Hardness Shore D of the unsaturated polyester base matrix composite.

Table 3 and **Figure 7** portray the relation between the percentage of water absorption and the weight fraction of PSZ that was supplemented to the unsaturated polyester resin base matrix composite. And, the outcomes indicated that the percentage of water absorption rises with raising the weight fraction of the particles of PSZ as well as attains its highest value 0.3% with the 3%wt. and 6%wt. addition of PSZ, while the minimum percentage of water absorption was 0.17% at 1% wt. of PSZ addition, compared with the percentage of the water absorption of the reference sample 0.21%. The water absorption conducts of the polymer packed composites at a specific ecological state being obtained via numerous parameters, like the methods of treatment, the features of matrix-filler, the composites composition, and the immersion period in water (Ramakrishna and Rai, 2006). An increase in the water absorption means that the open porosity will increase, and that will encourage the bone growth through the implant, which results in a rise in the implant mechanical fixation with the in-vivo living tissue.

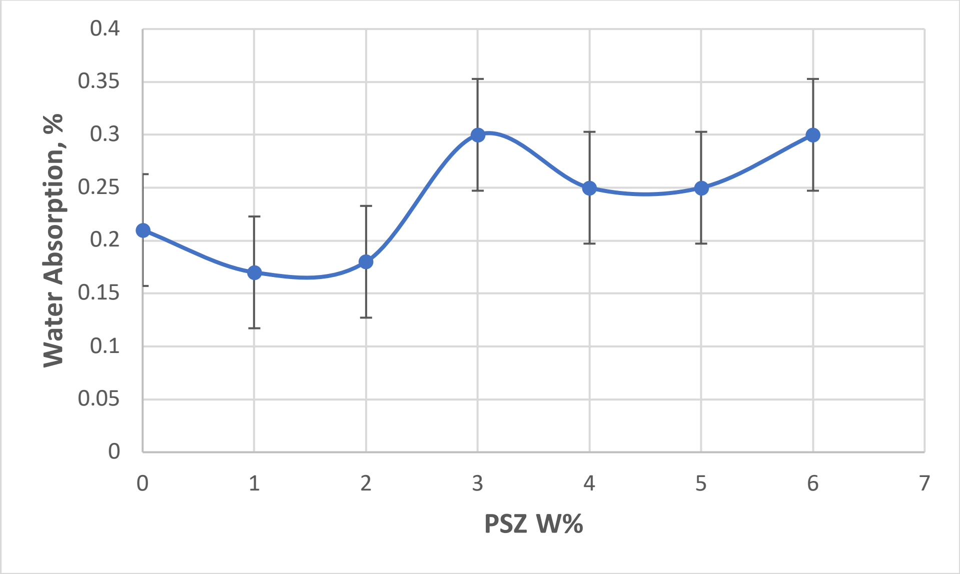

Figure 7. Effect of the PSZ addition upon the Water Absorption % of the unsaturated polyester base matrix composite

4. Conclusions

In this study, several properties were investigated in a biocomposite system based on unsaturated polyester resin containing PSZ in varying amounts (1%, 2%, 3%, 4%, 5%, and 6%) by weight. The results of this work revealed the following:

a) The 2% by weight PSZ ratio exhibited the highest tensile strength and elastic modulus (57 MPa and 1.45 GPa, respectively) compared to the reference sample (37.5 MPa and 0.8 GPa).

b) Elongation percentage decreased with the addition of PSZ to the unsaturated polyester. The highest elongation percentage was 6.75% at 2% by weight PSZ, compared to the reference sample, which had a higher elongation percentage (7%).

c) Certain properties, such as impact strength, hardness, and water absorption percentage, showed improvement at higher PSZ percentages. The 5% by weight PSZ ratio demonstrated the highest impact strength (3 J/mm²) compared to the reference sample (2.8 J/mm²). The 6% by weight PSZ ratio revealed the highest hardness and water absorption percentage (89 and 0.3%, respectively) compared to the reference sample (83 and 0.21%).

5. Recommendations for Further Investigations

a) Investigate the changes in fracture behavior as the PSZ filler content increases by using scanning electron microscope (SEM) and measuring the glass transition temperature (Tg) using the Differential Scanning Calorimetry (DSC) technique.

b) Examine the effect of particle size variation and surfactant addition on reducing surface tension and improving the wetting ability between PSZ and unsaturated polyester.

c) Porosity evaluation using Mercury Porosimetry.

d) Conduct a Hemolysis Analysis Test (ASTM F756-00) to determine the Hemolytic Index (HI), which serves as an indicator of blood biocompatibility.

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