U.P.B. Sci. Bull., Series B, Vol. 86, Iss. 3, 2024 ISSN 1454-2331

MECHANICAL PROPERTIES OF VISIBLE LIGHT CURED RESINS REINFORCED WITH NANOFILLERS IN THE PRESENCE OF COUPLING AGENT FOR DENTAL RESTORATION

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This study aims to develop dental nanocomposites based on SiO_2/ZrO_2/HA nanofillers and to evaluate their behavior. Surface treatment of nanofillers, including the reaction of 3-(methacryloyloxy)propyl trimethoxysilane (MPTMS) coupling agent was done in order to improve the compatibility of the phases, reducing the tendency to agglomerate, and hence improving the mechanical characteristics. Particles of varying sizes were distributed evenly between the groups. At separate times, nanofillers were treated with 1.5, 2.5 and 3.5 wt.% of coupling agent (MPTMS). The samples are made by mixing the monomer resin matrix with nanofillers. Dental nanocomposites treated with 2.5 wt.% MPTMS have considerably greater wear, and flexural than those treated with 1.5 and 3.5 wt.% MPTMS and based on this finding the compatibilization will be considered with this concentration. Experimentally developed dental nanocomposites with filler concentrations of 2.5%, 5%, 7.5%, 10%, 12.5%, and 15% wt.% are produced by polymerization in 60 seconds using the proper light curing system. Wear resistance, and flexural strength are measured and compared. The nanocomposite containing 10% filler exhibited superior mechanical characteristics to those containing 12.5% and 15% filler. Based on the results obtained, it was determined that the produced nanocomposites were suitable for tooth-filling applications.

Keywords: Mechanical properties, Bis-GMA, Functionalization agent, Dental restoration, Nanocomposite.

1. Introduction

In posterior teeth, longevity and survival studies continue to demonstrate that amalgam has a better track record than composites. Composite restorations on permanent teeth have a 7-year survival rate of 67.4% compared to 94.50% for amalgam restorations [1]. Flexural strength ranges from 80 to 120 MPa for dental

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composites, which can meet the needs of more minor repairs but cannot withstand major stress-bearing restorations. In contrast, dental amalgams possess flexural strength greater than 400 MPa [2, 3]. Numerous initiatives are underway to improve dental composite resins' clinical performance [4]. The filler content research has focused on particle size, loading, and silanization [5, 6] and developing novel particles [7, 8]. In contrast, research into the resin matrix has primarily focused on developing novel monomers [8, 9, 10]. Dental composites' physical qualities are very sensitive to particle size, filler quantity and surface chemistry. The hardness, compressive strength, elastic modulus, flexural strength, and polymerization shrinkage all are strongly influenced by the filler volume fraction [6]. In recent years, nanotechnology has played a vital role in developing composite dental materials. Nanotechnology employs both chemical and physical processes to design materials at the nanoscale, 0.1 to 100 nanometers in size [11]. Nanotechnology has emerged as the most significantly inspired field of technology [12]. These nanomaterials can be nanoparticles, nanoclusters, nanocrystals, nanotubes, nanofibers, nanowires, nanorods, etc., according to their various characteristics (size, shape, agglomeration, (self)assembly capacity, etc.). Several top-down and bottom-up manufacturing approaches have recently been utilized to produce nanomaterials [12]. Materials' optical, chemical, physical, and mechanical properties can be significantly enhanced by replacing bulk materials with nanoparticles [13]. Extensive research is being put into optimizing nanocomposites for specific uses in high-performance coatings, biomedical systems, structural materials, catalysts, photonics, and electronics. Composites with high mechanical properties are required for dental Class I and II posterior restorations, whereas composites with superior esthetics are required for anterior restorations. Unfortunately, a resin composite suitable for both posterior and anterior restorations has not yet been developed. Nanotechnology is having an increasingly profound effect on restorative dentistry with nanoscale fillers' ability to tailor the performance of composite materials for posterior and anterior advantageous uses [12, 13]. This article describes the development of a dental nanocomposite that possesses the aesthetic and mechanical qualities required for cosmetic restorations.

In the present study, a silanization coupling agent namely 3-(methacryloyloxy) propyl trimethoxy silane was utilized to modify the surface of the nanofillers (SiO_2, ZrO_2, HA). Following this, experimental dental nanocomposites are developed using various monomeric formulations and monomer-to-filler ratios. As a result, nanocomposites with varying mechanical properties were produced, demonstrating their usefulness and dependability for dental applications.

2. Experimental

2.1. Materials

The monomers that have been used are: Methylmethacrylate (MMA from Merck), Methacrylic Acid (MAA from HiMedia), 2,2- bis[4(2-hydroxy-3-methacryloyl propyloxy)phenyl] propane (Bis-GMA), Urethane- dimethacrylate (UDMA, USA), 1,6-hexanediol methacrylate (HDODA from Aldrich). The coupling agent that has been used is 3-(methacryloyloxy) propyltrimethoxysilane (MPTMS from Aldrich).

The nanofillers that have been used are: Zinc Oxide (ZnO) nanopwoder, Zirconium Dioxide nanopwoder (ZrO_2), Silicon Dioxide nanopowder (SiO_2); Hydroxyapatite (HA) all from Skyspring Nanomaterial. The photoinitiator that has been used is Camphorquinone (CQ from Aldrich). The accelerator that has been used is 2-(Diethyl amino)ethyl acrylate (DMAEMA from Aldrich)

2.2. Apparatus

A mechanical testing machine (LARYEE Co, China), working at 95 % confidence level was used by collaboration with the Department of Mechanical Engineering at Cape Peninsula University of Technology from Baghdad. The tool is made on a persistent speed of 6 mm/min that can do tensile testing at room temperature with a load cell of 20 kN and a cross-head speed of about 200 mm/min is used to analyze mechanical properties. The sample dimensions complied with ASTM D-412 specifications. The lamp radiates light within the range of 400 - 580 nm, that starts the cure of the substance. The commercially existing light supplies manipulated to assure the photo-polymerization provide the necessary blue radiation (~480nm).

2.3. Synthesis of resin nanocomposites

The nanocomposite series A and B involve different matrices (based on the nature of the monomers) but include identical fillers (Nano-ZrO_2, SiO_2, and HA). Each series has seven different groups, produced by combining the mixture of monomers with 10 wt% of Nano-ZrO_2, SiO_2, and HA fillers [14]. Zinc oxide (0.5wt%) was added to induce antibacterial activity. The following compounds are manipulated: 0.5 wt% CQ as an initiator and 0.5 wt% DMAEMA as accelerator. The nanocomposite was created in a glass container using magnetic mixing. The mixture is then placed within a stainless-steel mold of cylinder and surrounded on two sides (top and bottom) by pure, thin glass plates. The dimensions of the specimens are 2 mm high, 4 mm width, 25 mm length. The series consisted of two groups; each group was enhanced by nano-ZrO_2, SiO_2, and HA (nanofillers). Specimens were then irradiated for 60 seconds by the control manufacturer's instructions.

Table 1.

Precursors and composition of the monomers as well as photoinitiators that are used in developing the dental nanocomposite (A) (DNCA)

Sample No.	Bis-GMA (wt%)	UDMA (wt%)	MMA (wt%)	HDODA (wt%)	Nanofillers (10%) wt%	Initiator	Accelerator	Coupling agent
						CQ wt%	DMAEMA wt%	(MPTMS) wt%
A1	40	20	20	20	SiO_2	0.5	0.5	2.5
A2	40	20	20	20	ZrO_2	0.5	0.5	2.5
A3	40	20	20	20	HA	0.5	0.5	2.5

Table 2.

Precursors and composition of the monomers as well as photoinitiators that are used in developing the dental nanocomposite (B) (DNCB)

Sample No.	Bis-GMA (wt%)	UDMA (wt%)	MAA (wt%)	HDODA (wt%)	Nanofillers (10%) wt%	Initiator	Accelerator	Coupling agent
						CQ wt%	DMAE MA wt%	(MPTMS) wt%
B1	40	20	20	20	SiO_2	0.5	0.5	2.5
B2	40	20	20	20	ZrO_2	0.5	0.5	2.5
B3	40	20	20	20	HA	0.5	0.5	2.5

2.4. Characteristics of the samples' mechanical performance

Flexural characteristics

The flexural strength (σ), as well as the flexural modulus (E), were determined according to the ISO178 in the tests of 3-point bending through the use of a universal testing machine LARYEE Co. (China) [15]. Rectangular polymer samples (length x width x thickness: 80mm x 10mm x 4mm) were cut from the moulds according to the geometry mentioned above. E, as well as σ, were computed correspondingly using the formulas below:

$$E\ (\text{MPa}) = \frac{P1l^3}{4bd^3\sigma} \tag{1}$$

$$\sigma\ (\text{MPa}) = \frac{3P1}{2bd^2} \tag{2}$$

where, maximum load is denoted by P, the span between supports by l, the point in the stress-strain diagram where the elastic area is identified by P1, the thickness of the specimen by d, and the width by b.

Wear resistance

The wear resistance is evaluated at 37°C and for 48h. At 1.2Hz, 100000 cycles were tested according to **ASTM D406**. The stainless-steel balls (2.4-millimeter radius, Minor Parts Inc.) were employed as antagonists.

3. Results and Discussions

3.1. Effect of the amount of nanofiller on the mechanical properties

To produce dental nanocomposites, nanofiller (SiO_2) is utilized. For various concentrations of filler (2.5%, 5.0%, 7.5%, 10%, 12.5%, and 15% wt%), flexural strengths and as well as wear resistance were evaluated. Moderately light-filled formulations “up to 10 wt% of fillers” are subjected to characterization via significantly increased shrinkage compared to the other samples. However, the mechanical characteristics decline with increasing filler concentrations (12.5% and 15% by weight. Micro-dispersion optimization is crucial for producing desirable mechanical characteristics, and this was achieved primarily through establishing strong connections between the nanofiller and the polymer.

It is expected that the flexural strength and wear resistance will improve with increasing nano-filler content. This is because nanofillers were predicted to have the most robust interphase interactions between fillers and polymer chains due to their potent chemical characteristics, surface activity, and non-uniform association with the porous surface. Improved flexural strength and abrasion resistance are commonly attributed to changes in the polymer phase. The filler contact level and polymer determine the degree of reinforcement. The interaction forces would rise with increasing Nano-filler concentrations and levels of reinforcing [16].

As the concentration of nanoparticle filler increases, the material's hardness, flexural strength, and wear resistance improve because of enhanced interactions between the polymer matrix and filler. The more filler is added, the more extensive the formations associated with the physical linkages between polymer chains and filler particles, and the less mobile the molecules become. Hardness, wear resistance, and flexural strength would decline with filler loadings above 10% as the matrix becomes increasingly reinforced. Nanofillers have the lowest hardness, flexural strength, and wear resistance because of their agglomerated particle sizes and weak interactions between the polymer matrix and the fillers. These results indicate that the mechanical properties of dental composites are significantly affected by the mean agglomeration sizes of particle

It is also specified that the insertion of (SiO_2)-containing nanofillers into the polymer matrix can enhance dental nanocomposites' chemical and mechanical characteristics. Figs. (1 and 2) depict the gradual increase in mechanical parts of dental nanocomposites with increasing nanofiller content. The increased wear resistance and flexural strength of dental nanocomposites subjected to a (10 wt%) loading indicated the nanofillers super reinforcement. When the nanofiller level exceeds 10 wt. %, the mechanical characteristics develop lower due to the insufficient dispersion of the partial and multilayered nanofiller.

High interfacial shear strengths between the polymer matrix and nanofillers are formed due to the creation of supramolecular bonds and crosslinks that encapsulate nanofillers, improving mechanical properties. In addition, the matrix and nanofiller may prevent crack formation by adhering more strongly to one another. Efficient stress transfer from resins to nanofillers is required for maximum flexural strength, while increasing the filler volume fraction is necessary for maximum hardness [17]. The stiffness of composite material is extremely sensitive to the loading of its constituent particles. In contrast, the strength of the material is intended to be affected by the load transfer between the filler and matrix. However, the filler's particle form disproportionately impacts some dental composite's mechanical properties. Thus, it's essential to pay close attention to it.

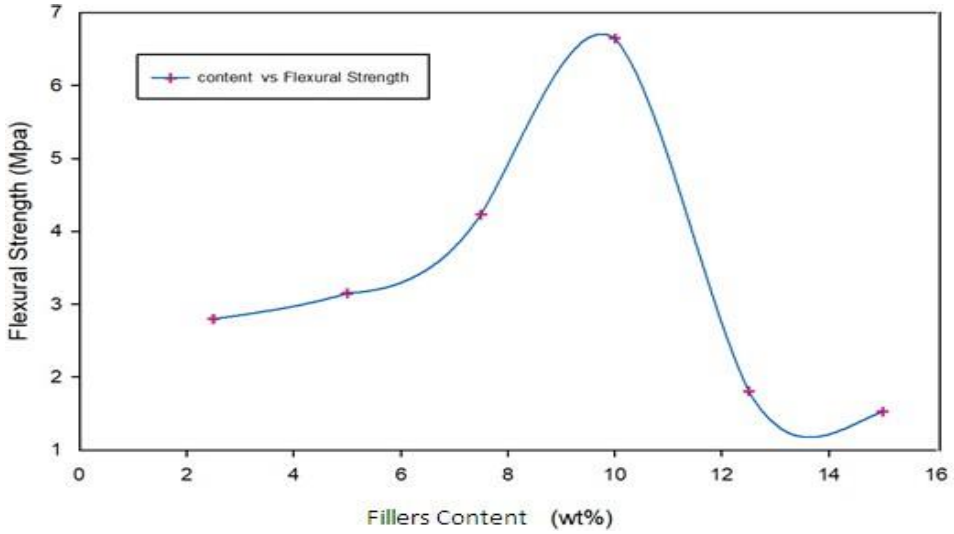

Fig. 1. Flexural strength of different concentrations of (SiO_2) nanofillers treated with 2.5 wt% of coupling agent (MPTMS)

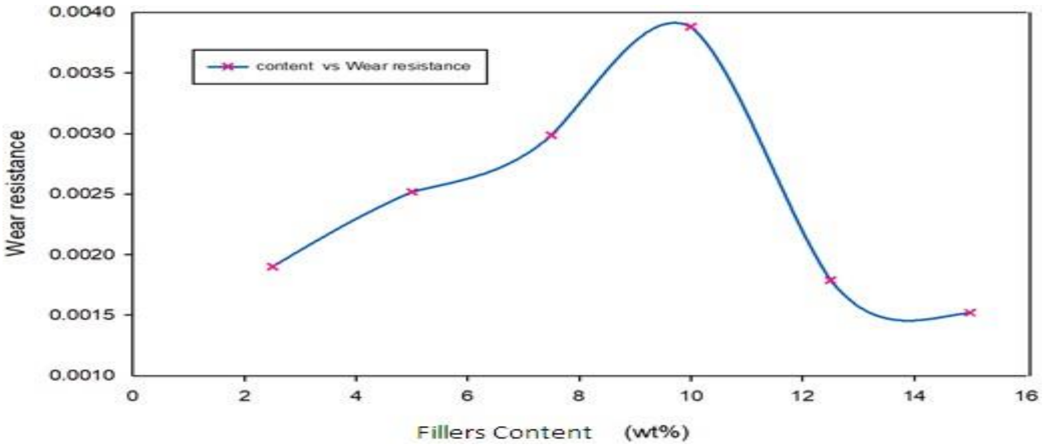

Fig. 2. Wear resistance of different concentrations of (SiO_2) nanofillers treated with 2.5 wt% of coupling agent (MPTMS)

3.2. Functionalization with MPMTS

Figs. 3 and 4 depict the effect of the amount of MPTMS employed for the silanization of the silica nanopwoder (3-4). It is evident from these data that functionalization with MPTMS increases flexural strength and wear resistance. This effect results from a stronger bond between the functionalized nanofiller and the polymeric matrix. Based on mechanical characteristics, it was determined that the best functionalization of the fillers occurs at 2.5 wt% MPTMS, where both flexural strength and wear resistance are maximized.

It was seen that the flexural strength of nanofillers “treated with 2.5 wt% MPTMS was considerably more significant than those treated with 1.5 wt% and 3.5 wt% MPTMS”. Identical outcomes were found in comparison to untreated nanofillers. All of these results demonstrate that functionalization enhances the compatibility between the matrix and the filler. If the silanization agent content exceeds 2.5%, the mechanical characteristics of composite materials pretreated with MPTMS will considerably decrease, even lower than the strength of the sample obtained with untreated silica.

3.3. Flexural strength

The primary goal of this research is to determine the optimal nanofillers content for increasing the flexural strengths of composite samples (SiO_2, ZrO_2, and hydroxyapatite). In Fig. 5, one can see that the nature of nanofillers has a significant impact on the flexural strength of composites containing nanoparticles. However, when filler addition values grow, strength values fall down. To circle back to the flexural strength findings, it's important to remember that interfacial contact strength is a significant determinant of the mechanical characteristics of composite materials. That is to say; poor interfacial connections impede insufficient stress transfer between parts. As a result, adding filler particles is likely to increase the number of weak links and reduce the strength of the material. The reduced strength and restricted movement of macromolecules in the matrix lead to an increase in power. To a large extent, the filler- rich values can be attributed to the overwhelming effect of poor filler/matrix coherence [18].

The nanocomposites with treated nanofillers had higher flexural strength than those with untreated nanofillers. This is due to the superior adhesion of treated nanofillers to the matrix, as seen in Fig. 5.

It was vital to remember that the filler fraction values in the nanofiller composite samples developed in this study are smaller than those in nano-size filler composites. The data presented here on the mechanical characteristics of models including Nano- sized filler shows that the mechanical properties of dental restorative composite samples were significantly enhanced using of nano-size nanofillers, despite the decreased weight fraction. There are several contributing aspects, but the most important one is the filler's good adherence to the polymer matrix at the Nanoscale. Group (B) has a slightly higher mean flexural strength than Group (A).

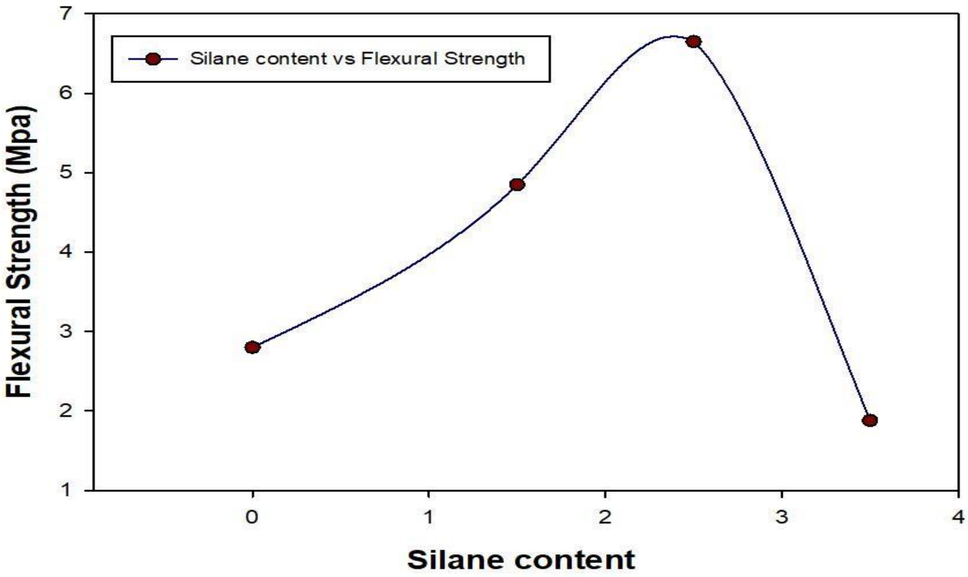

Fig. 3. Flexural strength of DNC (A) loaded with SiO_2 nanofiller treated with different concentrations of coupling agent (MPTMS)

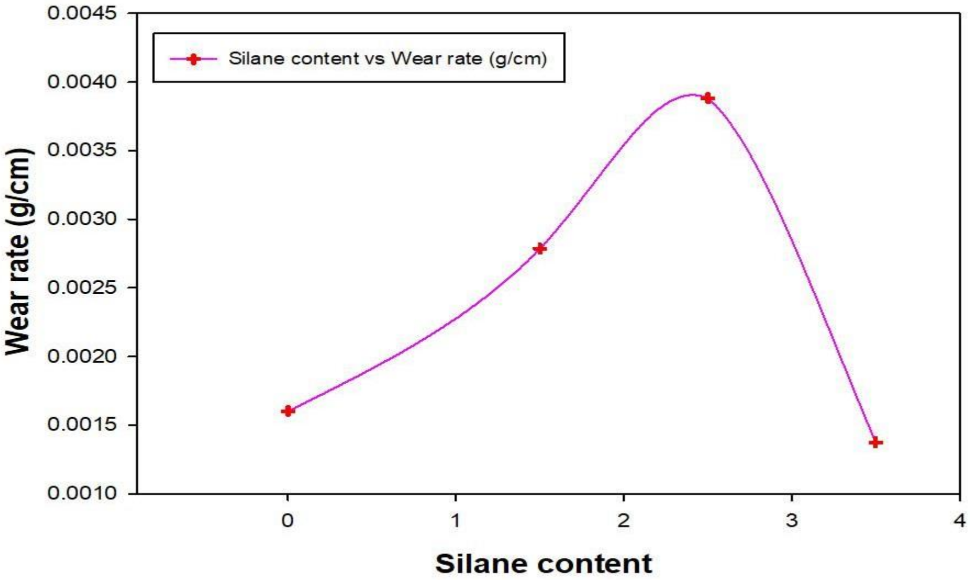

Fig. 4. Wear resistance of DNC (A) loaded with SiO_2 nanofiller treated with different concentrations of coupling agent (MPTMS).

This is due to the tight bond between the nanoparticles and the resin matrix and the nanoparticles' inherent ability to delay the development of cracks inside the dental composite matrix via the strengthening mechanism. The flexural modulus and tensile strength of composite dental nanoparticles are increased when nanoscale HA, SiO_2, and ZrO_2 are added. This characteristic is due to the creation of physical cross-link connections covering or shielding the nanoparticles (HA, SiO_2, and ZrO_2), which results in high shear strength of the interface between the resin matrix and the nanoparticles.

In addition, solid interface bonding between the resin matrix and the reinforcing nanoparticles is connected with producing a robust nanocomposite material structure (HA, SiO_2, and ZrO_2). This resulted in creating of composite materials with solid physical bonds, necessitating high flexural stress for failure and increased flexural modulus and strength.

It has also been shown that the addition of nanoparticles significantly changes nanocomposite specimens' flexural modulus and strength. It has been observed that the flexural strength of DNC (B) group nanocomposites loaded with SiO_2 nanofiller is greater than that of their corresponding DNC (A) group nanocomposites. The nanocomposites obtained by using SiO_2 nanopowders has greater flexural strength than the analogs with HA, ZrO_2 nanopowders [19].

In contrast, the results demonstrated that the composites reinforced with silica nanoparticles had the highest flexural strength, followed by hydroxyapatite and zirconia. This is owing to the tiny particle size of silica and hydroxyapatite fillers (10- 20 nm) and 25nm, respectively. These particles' enhanced contact surface area with organic resin adds to the higher mechanical strength [20].

Fig. 5 depicts the flexural strength test results for the six samples from DNC (A) and DNC (B). The influence of the MPTMS coupling agent in Nanofillers (ZrO_2, HA, and SiO_2) on the flexural strength of Nanocomposites may be inferred from these results. It is observed that the flexural strength of nanofillers treated with 2.5 wt% MPTMS silanization agent is more significant than that of nanofillers treated with 1.5% and 3.5% MPTMS.

3.4. Wear Resistance

Wear resistance for DNC (B) composite has been verified to be substantially stronger than wear resistance for DNC (A). The particle size of fillers can determine the results of wear. Specialists assume that complexes with smaller filler particles show greater resilience to wear. When the nanofillers (ZrO_2, SiO_2, and HA) content increases, the wear resistance of the dental nanocomposites decreases [21].

Wear resistance is improved by the incorporation of the MPTMS treated silica. That might be explained considering that treated nanofillers have better adherence to the polymer matrix, at a content of up to 2.5% modification agent followed by which, the wear resistance went down as the MPTMS silane content reach 3.5%. Consequently, the best wear resistance was found in the nanocomposite at a weight percentage of 2.5%.

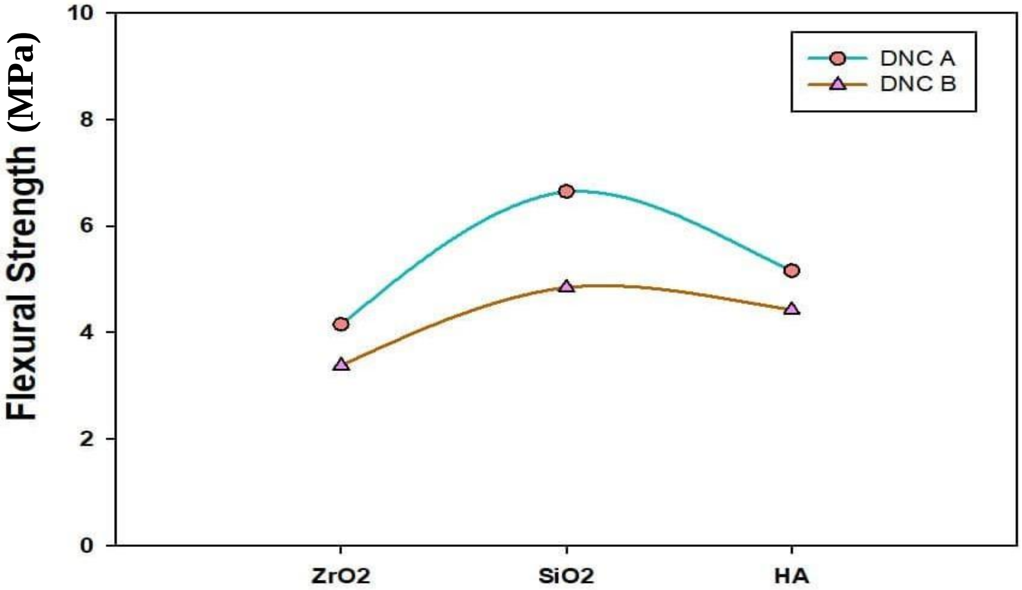

Fig. 5. Flexural strength of the DNC (A and B) loaded with treated nanofiller (SiO_2, ZrO_2, and HA) functionalized with 2.5 wt% MPTM

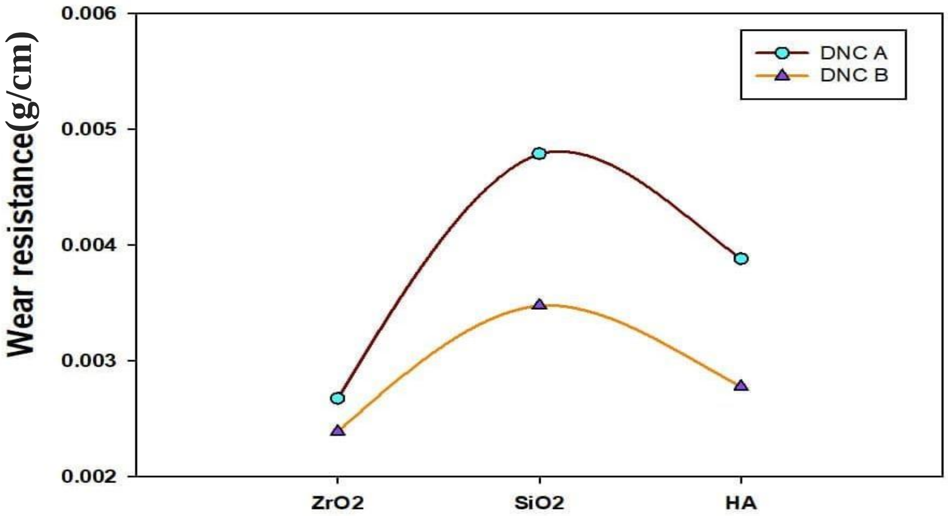

Fig. 6. The wear resistance of DNC (A and B) loaded with 2.5 wt% MPTMS treated nanofiller (SiO_2, ZrO_2, and HA).

1,6-hexandioldimethacrylate (HDODA) is utilized in accompanying with acrylate monomers as well as Bis-GMA, that can react with other molecules to form very large polymer molecules. The essential feature of a monomer is the polyfunctionality, the capacity to form chemical bonds to at least two other monomer molecules, as well as that improves the degree of cure of matrix of polymer, as well as a consequence, the resistance to wear. Special molecules known as functional monomers provide a polymer with additional, enhanced performance effects and/or significantly improve processing performance when incorporated in the polymerization process. Thus using appropriate nanoparticles (like SiO_2, ZrO_2 and HA) with specific size, an optimal loading can be obtained after which a drop in the nanoparticles spacing and a drop in the wear occurs [22].

4. Conclusions

The wear resistance and flexural strength of dental nanocomposites are well influenced by the MPTMS surface modification of the nanofillers (SiO_2, ZrO_2, HA). Dental nanocomposites suffer from poor dispersion and weak mechanical properties when untreated fillers are used and directly are dispersed within the monomers. Wear resistance and flexural strength can be improved if modified SiO_2, ZrO_2 or HA nanoparticles are used to develop the dental nanocomposites. Concerning particle size, samples with larger nanoparticles and other particles exhibiting agglomeration exhibited worse mechanical characteristics. Conversely, a positive link between hardness levels and wear resistance is shown. Using MPTMS-modified fillers, nanocomposites with improved flexural strength and wear resistance were produced.

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