Research Article

Effects of Silica Nanoparticles and Silica-Zirconia Nanoclusters on Tribological Properties of Dental Resin Composites

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Roughness and hardness are among the most important variables in the wear (resistance) performance of dental resin composites. In this study, silica nanoparticles and nanoclusters of silica and silica-zirconia nanoparticles were evaluated for use as reinforcement agents in dental resin composites. Nanoclusters with spherical morphology were obtained from aqueous dispersions of nanoparticles by spray drying. Roughness was measured through atomic force microscopy (AFM) while nanohardness was evaluated by nanoindentation. The roughness values obtained with silica nanoparticles were lower (22.6 ± 6.6 nm) than those obtained with silica and silica-zirconia nanoclusters (138.1 ± 36.6 nm, 116.2 ± 32.2 nm, resp.), while the hardness values of all composites were similar (nanoparticles = 0.24 ± 0.01 GPa, silica nanoclusters = 0.25 ± 0.04 GPa, and silica-zirconia nanoclusters = 0.22 ± 0.02 GPa). Based on this study, it can be established that particle size is a determining factor in the roughness of the final material, while the key variable for nanohardness was the concentration of the reinforcement materials.

1. Introduction

Composite dental materials are widely used to repair anterior and posterior teeth due to their ability to replicate natural dental structure, workability, mechanical properties, and clinical performance [1–3]. Wear resistance is an important property in the performance of dental composites because lack of wear resistance will produce an excessive reduction in structure, resulting in the loss of posterior tooth support, vertical dimension of occlusion, masticatory efficiency and esthetics, as well as alterations in the functional path of masticatory movement, fatigue of masticatory muscles, and faulty tooth relationship [4]. Wear (resistance) performance of dental resin composites is affected by roughness and hardness, while roughness also influences aesthetic appearance, discoloration, plaque accumulation, the appearance of secondary caries, gum inflammation, and wear of opposing and adjacent teeth [5–8], and hardness,

defined as how resistant the material is to penetration, can be used to predict wear resistance and the tendency of the material to erode the opposing tooth or material [7, 9, 10].

It is accepted that roughness, being caused by the loss of particles, is reduced when the particle size is decreased [11]. Finer particles for a fixed-volume-fraction have been shown to result in decreased interparticle spacing and thereby reduced wear of dental composites [12]. This indicates that there is a relationship between roughness and wear resistance: lower roughness being related with an increase in wear resistance. Meanwhile, wear resistance tends to increase with increasing hardness, but quantitative relationships between wear resistance and hardness have not been established, with some studies finding a direct correlation and others not [4]. This may be due to the fact that hardness is an intrinsic property of the material, which depends only on composition and microstructure, while abrasion resistance is not an intrinsic property, since it may also depend

on variables such as the testing technique used, the abrasive properties, and environmental conditions [13]. Therefore, hardness is a parameter that is related to wear resistance but, due to other variables that affect it, there is not a direct relationship in all cases. In general, the literature reports that hardness increases with the quantity of filling [7, 10, 14–16]. However, it is not necessarily the case that a larger quantity of filling causes an increase in the hardness of the material or generates an increase in wear resistance. This is because hardness also depends on the type and quantity of the silanization agent, the method of surface modification [17], the dispersion degree of nanoparticles, the particle size, and the hardness of the filler particles, since harder particles exhibit higher surface hardness in the composite [18].

As particle size is related to roughness, hardness, and other properties, it is proposed that the use of nanofillers will allow materials to be obtained with better mechanical properties such as compression, fracture, and bending resistance [19–21] and improved surface properties such as better gloss, polish, and wear resistance [5, 6, 22–24]. It is also proposed that the use of nanoparticles will allow reduced roughness [6], although other studies have pointed to a lack of evidence supporting this, since the difference in measuring methods and processes for polishing makes it difficult to compare them [11]. There are reports that indicate that nanoclusters, in spite of having bigger particle size than individual nanoparticles, allow materials to be obtained with improved surface properties such as better gloss, polish, and wear resistance [5, 6, 22–24]. Nanoclusters are nanoparticle aggregates with controlled size and morphology, obtained prior to the dispersion process in the resin [25–27]. One of the methodologies used to obtain these aggregates is spray drying using nanoparticle dispersions [28–30]. Examples of dental materials that use nanoparticle aggregates are Filtek Supreme Body resins and Filtek Supreme Translucent resin (3M), which use aggregates of silica and zirconia nanoparticles [23, 25]. These aggregates are approximately 760 nm in size and are used in the materials in combination with nonaggregated silica nanoparticles [22, 24]. Nanoclusters have been proposed as an alternative to nanoparticles, in order to solve problems such as excessive increase in the viscosity of the composite material before it is polymerized [19], and the tendency of nanoparticles to agglomerate due to their high surface energy, preventing nanomaterials with nonaggregate nanoparticles being obtained [19]. With regard to hardness, studies report improved hardness on the part of microparticles at relatively higher concentrations than nanoparticles, and high hardness values for dental composites reinforced with nanoparticles [18], but there is a lack of evidence about differences in hardness between composites that use nanoparticles or nanoclusters.

The objective of this study is to correlate the properties of roughness and hardness with the use of nanoparticles and nanoclusters, in order to provide information facilitating the use of reinforcement agents of this nature in dental resin composites. Our hypothesis is that lower roughness is obtained with nonaggregate silica nanoparticles than with nanoclusters, while hardness is similar in both cases. For the

purpose of this study, spray drying was used to obtain nanoclusters of silica and silica-zirconia. This kind of nanoclusters was chosen because they are used in commercial dental composites. Composites of nonaggregated silica nanoparticles, silica nanoclusters, and silica-zirconia nanoclusters were prepared. The roughness of these materials was evaluated by atomic force microscopy (AFM) and their nanohardness by nanoindentation.

2. Materials and Methods

2.1. Materials.
For dental resin composites, the following kind of nanoparticles were used: silica in an aqueous dispersion (20% by weight of nanoparticles), with a pH between 2 and 4, brand name SNOWTEX® ST-OL, made by Nissan Chemical (USA), and zirconia in an aqueous dispersion (30% by weight of nanoparticles), pH 3, brand name NanoUse® ZR 30-AL, made by Nissan Chemical (USA). Silica nanoparticles were functionalized by methacryloxypropyltrimethoxysilane (MPS) (97%) (Alfa Aesar).

The monomers were bisphenol A glycidyl methacrylate (Bis-GMA) (90%), bisphenol A polyethylene glycol diether dimethacrylate (Bis-EMA) (90%), urethane dimethylacrylate (UDMA) (90%), and triethylene glycol dimethacrylate (TEGDMA) (90%). These were acquired from Esstech (USA).

Polymerization initiation system was composed by ethyl 4-(dimethylamino) benzoate (4EDMAB) (99%) provided by Alfa Aesar and (CQ) Camphorquinone (97%) provided by Sigma Aldrich.

2.2. Methods

2.2.1. Characterization of Silica and Zirconia Nanoparticles.
Morphology of the silica nanoparticles was determined using a S4700 scanning electron microscope (Hitachi, Japan). An Au/Pd alloy particle coating of approximately 2 nm thickness was deposited on the sample, using a sputtering device. All the samples were analyzed at a work distance of 5 mm and a voltage of 15.0 kV.

The morphology of zirconia particles was determined using a 2010LAB$_6$ transmission electron microscope (TEM) (Jeol, Japan). For this analysis, the dispersion was diluted in ethanol. After this, a drop of each dispersion was deposited in a TEM grid, allowing the water and ethanol to evaporate. The samples were analyzed using a voltage of 200 kV.

The ζ potential measurements of the silica and zirconia nanoparticles were performed using the light scattering technique, for which Zetasizer Nano ZS equipment (Malvern Instruments, UK) was used. Before each measurement, the particle dispersion was diluted using distilled water.

2.2.2. Functionalization of Silica Nanoparticles.
Functionalization of silica nanoparticles was carried out by heating a suspension of silica nanoparticles (20 wt.%) in the presence of MPS at 65°C for 30 hours under constant stirring. The weight percent of MPS required for nanoparticle silanization was calculated according to the following equation [31]:

$$X = \left(\frac{A}{w}\right)f, \qquad (1)$$

where A is the surface area of the silica in m^2/g, which is $76.3\,m^2/g$ [32], w is the surface coverage by gram of the silanization agent, which for MPS is $2525\,m^2/g$ [31], and f is the quantity of silica in grams. Taking into account these values, to cover 1 gram of silica (f), 0.03 g of silanization agent, or 3% by weight with respect to the weight of the silica, is required. In order to have an excess of functionalizing agent and thereby generate better coverage, 4% by weight was used with respect to the silica. The nanoparticles functionalized were dried at 80°C in a vacuum oven for 24 h and were analyzed by infrared spectroscopy in FT-IR Spectrum One equipment (Perkin Elmer, USA), using the KBr pellets method. The average spectrum reported was obtained from 16 scans at a resolution of $4\,cm^{-1}$. The thermic degradation of the functionalized silica nanoparticles was studied by thermogravimetric analysis, applying a heating rate of 10°C/min between 30 and 800°C in air. The weight loss was recorded as a function of time and temperature using TGA Q500 equipment (TA Instruments, USA).

2.2.3. Production of Nanoclusters

(1) Silica Nanoclusters. Silica functionalized aqueous dispersion (20 wt.%) was dried using a B290 Mini Spray Dryer (Büchi, Switzerland) to obtain silica nanoclusters. The drying conditions were air temperature at the entrance of the dryer of 180°C, air temperature at the exit of the dryer between 70 and 80°C, air flow at the nozzle of 600 L/h (50% of the nozzle rotameter scale), drying air flow of $30\,m^3/h$ (75% of the dryer scale), and pump speed of 5 mL/min (15% of maximum speed).

(2) Silica-Zirconia Nanoclusters. The silica-zirconia nanoclusters were obtained using an aqueous dispersion (20 wt.%) of functionalized silica nanoparticles (obtained as described in Section 2.2.2), and an aqueous dispersion (30 wt.%) of zirconia nanoparticles. A blend with 8.3 wt.% by weight of nanoparticles (30 wt.% were zirconia) was stirred using a paddle agitator set to 600 rpm for 30 minutes before drying. The drying was performed using a B290 dryer (Büchi, Suiza) under the same conditions used to obtained the silica nanoclusters.

2.2.4. Characterization of Silica and Silica-Zirconia Nanoclusters.
The particle size distribution of the nanoclusters was evaluated by static light scattering using Mastersizer 2000 equipment (Malvern Instruments, UK) and the Hydro 2000 accessory. Morphology of nanoclusters was determined using a S4700 scanning electron microscope (Hitachi, Japan), using the same procedure employed to analyze silica nanoparticles morphology.

2.2.5. Nanoparticles and Nanoclusters Dispersion

(1) Dispersion of Silica Nanoparticles. To obtain a dispersion of nonaggregated functionalized silica nanoparticles, an aqueous dispersion of said particles (20 wt.%) was put into contact with the monomer mix (TEGMA:UDMA:Bis-EMA: Bis-GMA, 0.3 : 0.7 : 1 : 1 respective weight ratios), containing 0.2% CQ and 0.8% 4EDMAB, based on the weight of the monomers. The quantity of this mixture was determined taking into account the expected concentration of silica nanoparticles at the end of the process (i.e., 30 wt.%). The mixture was subjected to heating at 50°C and stirring using a BDC 3030 stirrer (Caframo, USA), with paddles inclined at 45°, working at 350 rpm for 40 minutes, then 450 rpm for 10 minutes and finally 750 rpm for 23 hours and 10 minutes. This is a variation of a methodology performed in our laboratory and previously reported [26], and the difference is that the system in this investigation used an aqueous phase and an organic phase, while in the previously reported methodology, only an organic phase was used.

(2) Dispersion of Silica and Silica-Zirconia Nanoclusters. The dispersions of nanoclusters (30 wt.%) were obtained by its manual dispersion in the monomer blend, TEGMA:UDMA: Bis-EMA:Bis-GMA, 0.3 : 0.7 : 1 : 1 respective weight ratios, containing 0.2% CQ and 0.8% 4EDMAB, based on the weight of the monomers.

2.2.6. Tribologial Properties

(1) Roughness. Test cylinders of 4 mm diameter and 2 mm thickness were prepared using a metallic mold. The cylinders were photopolymerized by overlapping irradiation for 60 s on the two circular faces, using a Sunlite 1275 light curing lamp (FEN Dental, USA) with a light source of 450−490 nm. The cylinders were then placed on a stainless steel metallic disc of 12 mm diameter and polished with Ecomet III equipment (Buehler, USA), using panels embedded with a dispersion of diamond particles of 15, 6, 1, and 0.25 μm.

Roughness measurements were performed using a MFP-3D device (Asylum Research, USA). The relative heights map was obtained in air atmosphere in intermittent contact mode with a Tap300Al-G-10 reference point (NanoAndMore, USA), with a nominal spring constant of 40 N/m and a fundamental resonant frequency of 300 kHz. The scan was performed in an area of 90 square microns, and 4 cylinders per sample were used.

(2) Nanohardness. Test cylinders similar to those used for the roughness analysis were used. The nanoindentation measurements were performed with a TI-950 device (Hysitron, USA), using a Berkovich tip with a nominal radius of 50 nm. The measurements were taken in air atmosphere at room temperature, under the load control mode. Load and unload speeds were 1 mN/s and 0.5 mN/s, respectively, with pauses of 60 s at a maximum load of 5 mN. To obtain the exact area function of the indenter, the system was calibrated using a standard of quartz with an elastic modulus of 73 GPa and a Poisson ratio of 0.17. Two cylinders per sample were analyzed, and 6 measurements were taken of each cylinder, for a total of 12 measurements per sample. The data analysis for

the determination of the nanohardness was performed using the Oliver and Pharr method [33].

2.3. Statistical Analysis. The results are expressed as the mean ± standard deviation. The normal distribution of each data set was confirmed using the Shapiro-Wilk test. The statistically significant differences between groups of data regarding the nanohardness and roughness were based on one-way variance test (ANOVA) followed by a post hoc Tukey test with 95% confidence (i.e., $p = 0.05$). The STATGRAPHICS centurion 18.1.01 software was used.

3. Results and Discussion

3.1. Characterization of Silica and Zirconia Nanoparticles. The average size of silica nanoparticles according to the product technical specification is between 40 and 60 nm. This is consistent with the particle size observed in the SEM micrograph shown in Figure 1. The particles are of spherical morphology, which is as expected for nanoparticles synthesized by sol-gel technology, given that this is a method that allows spherical monodispersed particles to be obtained [34]. Spherically shaped particles and a homogenous size distribution allow dispersions at high concentrations to be obtained, as shape and size homogeneity are factors that influence the viscosity of dispersions [35]. The spheres, due to their shape, can generate a kind of lubricating action on the material, allowing it to flow freely and having low impact on viscosity. Meanwhile, amorphous particles tend to obstruct the flow, thereby generating a greater increase in viscosity [35].

The colloidal silica particles in SNOWTEX-OL are negatively charged on their surface, according to reports in the literature [36]. The ζ potential measured was −54 mV which, added to the fact that silica sols present steric stabilization caused by the presence of oligomeric or polymeric silicate species at the interface [36], is indicative of the high stability of the dispersion of these nanoparticles [37]. This stability and nonaggregation of the particles in suspension is a factor, which will affect the dispersion grade of the particles when dispersed in the monomers blend. Dispersion degree affects the interaction surface area between the filler and the polymeric matrix. Lower aggregation permits higher surface area and interaction between filler and matrix, which affects roughness, as particle loss is reduced. Uniform dispersion of nanoparticles provides enough distance between the particles, increasing composite hardness [18].

The zirconia nanoparticles are aggregates of individual nanoparticles of lower size, as can be seen in Figures 2(a) and 2(b). Moreover, they possess amorphous morphology, as evidenced in Figure 2(a). The nanoparticle aggregates are between 40 and 100 nm in size according to the product technical specification, which is corroborated by TEM images. The primary nanoparticles of zirconium dioxide are approximately 5 to 10 nm in size, as shown in Figure 2(b).

The ζ potential analysis indicates that these aggregates have a positive surface charge, with a value of 43 mV. This is due to the low pH of the system, which causes protonation of
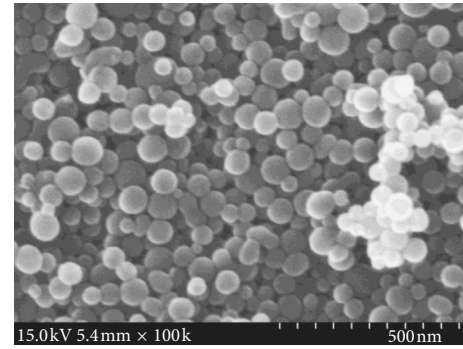

FIGURE 1: SEM micrograph of silica nanoparticles.

the ZrOH groups to $ZrOH_2+$ groups. This value indicates that the particles have high electrostatic stability [37].

3.2. Functionalization of Silica Nanoparticles. The functionalization of the silica nanoparticles does not affect their size or morphology, as shown in Figure 3, where both the shape and size of the nanoparticles are similar to those of the bare nanoparticles.

The FT-IR spectrum of the silica nanoparticles before and after being functionalized is shown in Figure 4. The bonds attributable to the extension vibrations of the C=C bonds (around $1630 \, cm^{-1}$), to the aliphatic C=O bonds (around $1700 \, cm^{-1}$), and to the C–H bonds (around $2950 \, cm^{-1}$) are due to the presence of MPS as the functionalizing agent. These bonds are not observed in the FT-IR spectrum of the bare silica nanoparticles. Thermic analysis of the particles functionalized with MPS indicated that the silanization grade was 1.5%, associated with the weight loss between 200 and 600°C. Silanization grade affects roughness and hardness. Silanization prevents the loss of surface particles because of the covalent bond between particles and matrix, and hardness depends on the type and quantity of the silanization agent as well as the method of surface modification [17].

3.3. Production of Nanoclusters. Figure 5 shows the particle size distribution of the silica and silica-zirconia nanoclusters obtained by spray drying. This shows that the average particle size of the silica nanoclusters is approximately 4.5 μm, with a distribution varying between 1 and 20 μm, while the silica-zirconia nanoclusters have an average size of 2.0 μm, with sizes between 0.2 and 10 μm. Hence, the size of the silica-zirconia aggregates is approximately half of that obtained for silica alone. Lower size of silica-zirconia nanoclusters is due to the reduction in the concentration of the silica-zirconia dispersion, along with the greater density and molecular weight of zirconium [28, 38]. This difference in size will affect roughness, as it is accepted that roughness caused by particle loss is reduced when particle size is decreased [11].

In Figure 6, it can be observed that both types of nanoclusters are of spherical morphology. When zooming in on the surface of the silica nanoclusters (Figure 6(b)), a relatively homogenous surface formed by nanoparticles
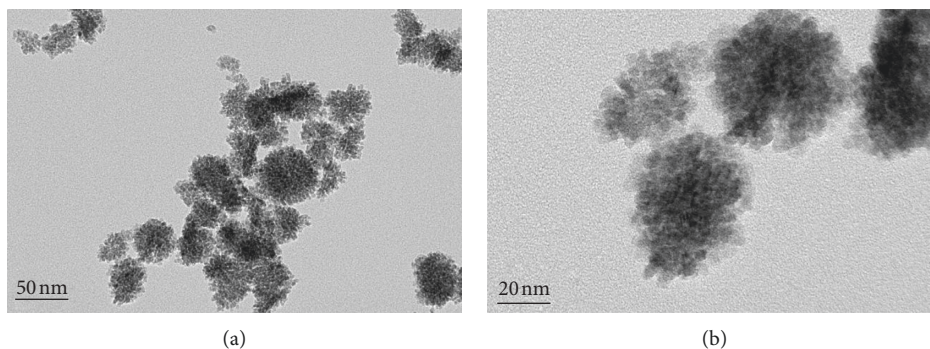
(a)

(b)

FIGURE 2: TEM micrographs of (a) zirconium dioxide nanoparticles and (b) close-up view of zirconium dioxide nanoparticles.
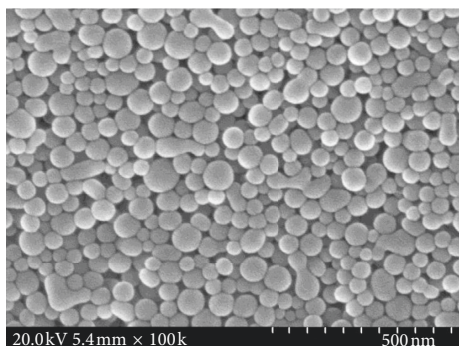

FIGURE 3: SEM micrograph of functionalized silica nanoparticles.
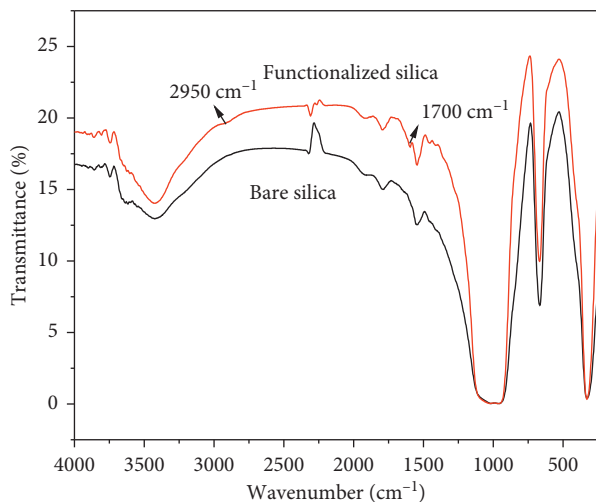

FIGURE 4: FTIR analysis of functionalized and bare silica nanoparticles.

FIGURE 5: Particle size distribution of the nanoclusters.

around 50 nm in size and organized in a hexagonal arrangement is observed, with the presence of individual particles not forming an integral part of the nanoclusters. These results are consistent with the sizes and morphologies found in another study [39] where aqueous silica dispersions were used to obtain aggregates by spray drying.

On the surface of the silica-zirconia nanoclusters (Figure 6(d)), the presence of zirconia nanoparticles causes a lower regularity of the hexagonal arrangement of the particles, due to their migration into the spaces left by the silica
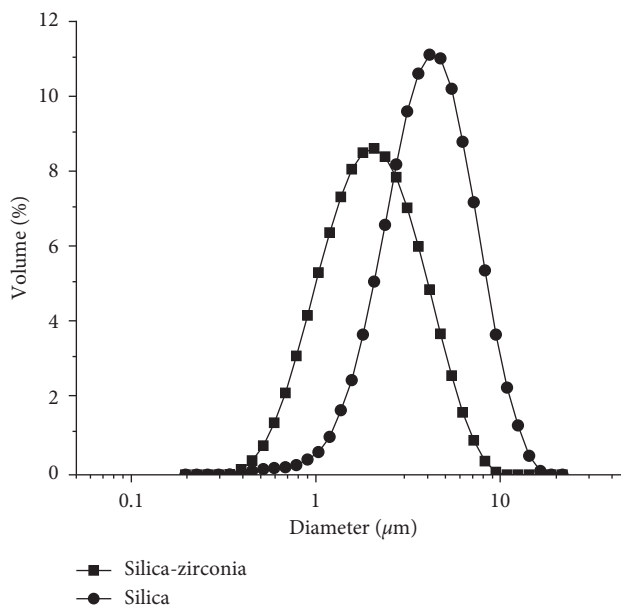
nanoparticles, reducing the porosity of the surface. In silica-zirconia nanoclusters, the opposing surface charge value (silica = −54 mV, zirconia = 43 mV) contributed to the homogenization of the particles when they were mixed and subsequently subjected to spray drying. This is because the zirconium dioxide particles tend to be surrounded by silica particles, and there is a low possibility of the zirconia nanoparticles encountering one another, a phenomenon also found in other studies [40]. This contributes to the zirconium dioxide nanoparticles being homogenously distributed in the nanocluster. This can be corroborated in the SEM images (Figures 6(c) and 6(d)), where a homogenous distribution of the zirconia in the nanoclusters can be seen. The homogeneity of zirconia inside nanoclusters will affect their behavior. This is because nanoclusters with only zirconia, or within which there is no homogeneity of zirconia, may show different roughness and hardness compared with nanoclusters obtained, as zirconia aggregates have a higher size than silica nanoparticles (40–100 nm vs 40–60 nm, resp.) and are not functionalized, and functionalization and size being factors that affect roughness and hardness.
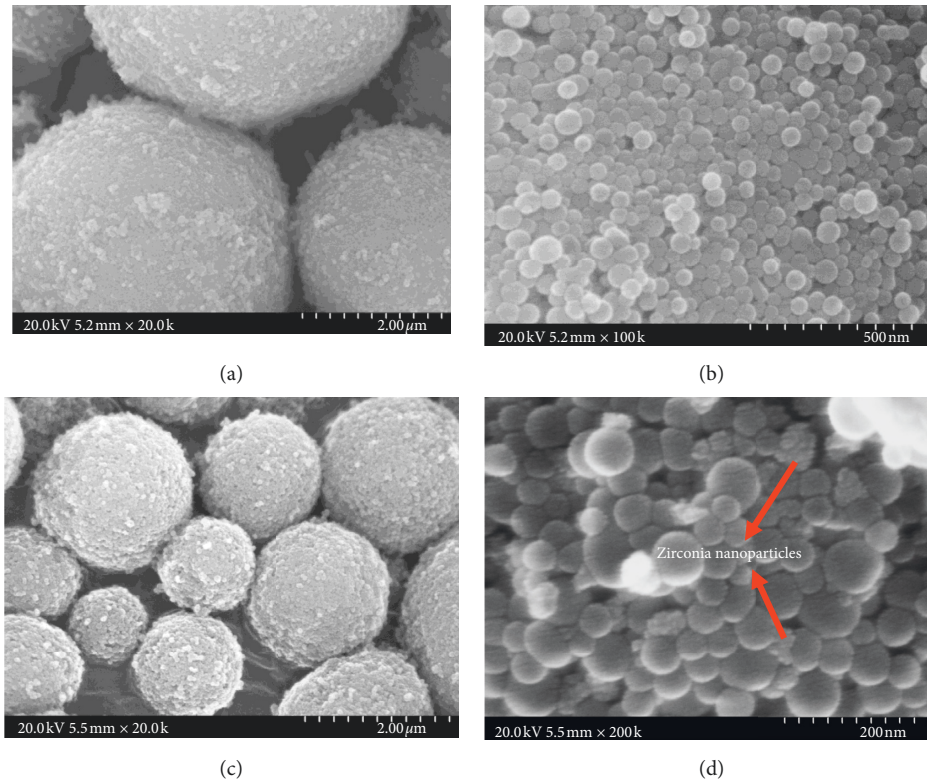
(a)

(b)

(c)

(d)

Figure 6: SEM micrographs of (a) silica nanoparticle nanoclusters, (b) surface of silica nanoclusters, (c) silica-zirconia nanoclusters, and (d) surface of silica-zirconia nanoclusters.

3.4. Dispersion of Nanoparticles and Nanoclusters.

Figures 7(a) and 7(b) show that silica and silica-zirconia nanoclusters had a good dispersion. In the AFM image shown in Figure 7(c), it can be seen that there is also an adequate dispersion of the silica particles in the polymeric matrix at 30 wt.%, since these can be individually observed. This shows how the solvent evaporation technique, along with the presence of the functionalization agent on the surface of the particles, allows dispersions of nonaggregated silica nanoparticles to be obtained, and that this condition continues even after polymerization. These results permit comparison between different kinds of materials, including both nonaggregate nanoparticles and nanoclusters, since aggregation could affect the roughness and hardness.

3.5. Tribological Properties

3.5.1. Roughness.

Figure 8 shows the results of the roughness analysis. Statistical analysis using the Tukey HSD test indicates that the samples with silica nanoparticles are statistically different from those that contain the nanoclusters ($p < 0.05$). Roughness is lowest when nonaggregated silica particles between 40 and 60 nm in size are used as reinforcement agent (22.6 ± 6.6 nm) and highest when the silica nanoclusters with an average size of 4.5 μm are used (138.1 ± 36.6 nm). There is no statistical difference between the two types of nanoclusters ($p > 0.05$); the average roughness value obtained is lower when silica-zirconia

nanoclusters with an average size of 2.0 μm are used (116.2 ± 32.2 nm vs 138.1 ± 36.6 nm). The results therefore show that there is a correlation between particle size and roughness, with lower roughness being obtained at lower particle size.

Some studies from the literature propose that the size has a significant effect on surface properties like roughness [11]. However, other studies posit that there is a lack of evidence for this statement [11]. This is because there are other factors affecting roughness such as the bond of the particles in the aggregates [41], as well as differences in measurement methodologies and polishing processes that make comparison between materials difficult [11], since the polishing technique affects the final roughness of the material [8, 42]. In this case, the comparison is valid, since all the materials were subjected to the same polishing process, and all have the same percentage of reinforcement material and the same polymeric matrix, without particles aggregation. Therefore, the changes can be attributed to the type of inorganic reinforcement. In this regard, it is important to consider that when relating the effects of the reinforcement material, the mechanical and tribological properties of the composite resins depend on the particle size, the structure of the nanoclusters, the bond mechanism between the particles and the polymeric matrix, and the nature of the bond between the primary particles in the nanoclusters. This last bond mechanism is responsible for micromechanical deformation behavior and fracture of structures in nanoclusters, especially in the case of spray-dried nanoclusters [41, 43]. Taking
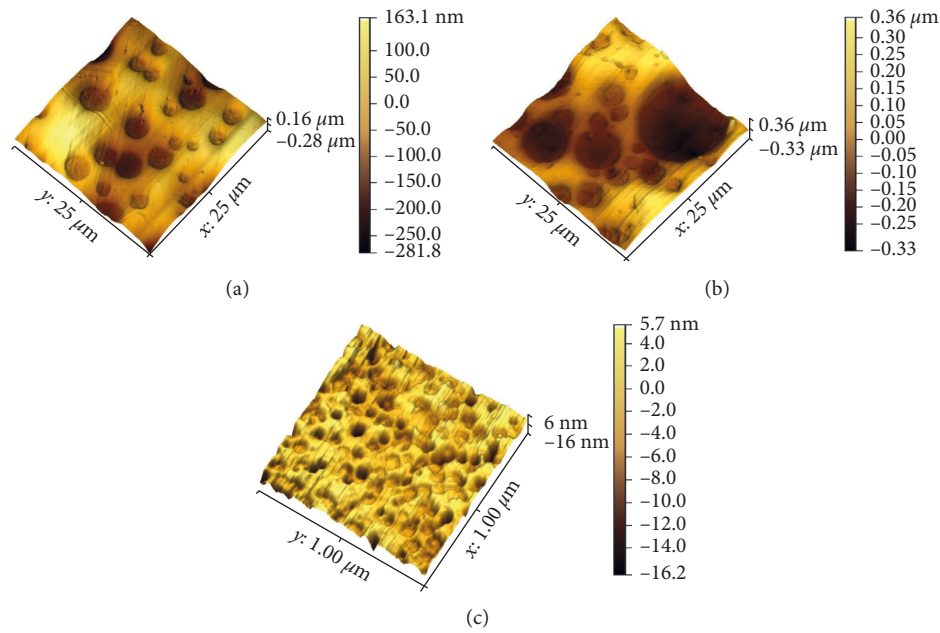
FIGURE 7: Images obtained by AFM. (a) Silica-zirconia nanoclusters, (b) silica nanoclusters, and (c) nonaggregated silica nanoparticles.
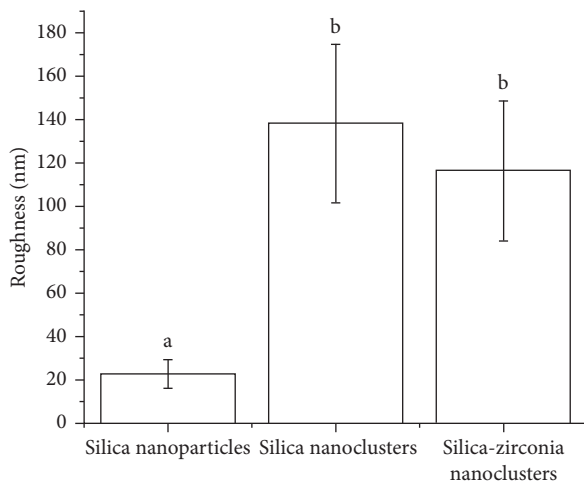

FIGURE 8: Roughness of materials reinforced with 30% by weight of particles. The letters indicate statistically homogenous groups (Tukey HSD test ($p > 0.05$)).

into account the above, inorganic reinforcement of the evaluated materials differs in size, morphology, and in the strength of the bond that exists between the reinforcement and the polymeric matrix. The nonaggregated silica particles bond to the polymeric matrix through chemical links generated by the presence of the functionalizing agent at the surface. The same type of bond exists between the silica aggregates and the polymeric matrix. However, in this case, the specific area available for bonding with the matrix is higher in nonaggregate silica nanoparticles than in nanoclusters. In nanoclusters, part of the surface area of the nanoparticles is occupied by the surface interaction between the nanoparticles inside the nanocluster. Moreover, in the case of the silica-zirconium dioxide aggregates, the presence

of zirconium dioxide negatively affects the bond to the polymeric matrix as these particles are not functionalized. This could have been an influential factor in the high roughness values obtained with these nanoclusters, which in spite of having lower particle size than silica nanoclusters, have similar roughness to them. For the nanoclusters, it is also necessary to take into account that the bond strength between the nanoparticles is low, as there is no chemical bond between them. This could allow the nanoparticles to become detached from the material more easily, affecting the roughness to a considerable degree. In these cases, the lack of chemical bond between the nanoparticles could be modified by submitting the aggregates to sintering with temperature, obtaining a higher level of cross-linking of the particles, leading to an increase in the bond strength and higher rigidity [43]. The above may explain why the results found in this study with nanoclusters are different to those reported for Filtek Supreme Body and Filtek Supreme Translucent resins (3M) [5, 20], where the aggregates were subjected to a sinterization process that caused a chemical bond of the individual particles [20], allowing lower roughness values to be obtained, as well as improved surface property values such as gloss and wear resistance [5, 6, 20, 24, 44].

Therefore, in this case, the behavior of the material was determined by the large size difference between the nonaggregated silica particles and that of the nanoclusters; the lower chemical bond between the particles and the matrix for the nanoclusters; and the lack of chemical union between the nanoparticles of the nanocluster. The results support the use of nanoparticles to obtain material with lower roughness, due to the fact that with a lower particle size, the surface alterations caused by the loss of particles are reduced [6]. This supports the growing use of nanoparticles in dental restoration resins, where roughness is an important parameter [6, 7]. Nanoparticle aggregates can be an alternative

option, but a chemical union needs to exist between the individual particles to improve their performance, and it is necessary to ensure a chemical bond of the aggregate to the polymeric matrix through functionalization.

3.5.1. Nanohardness. Figure 9 shows the results of the nanohardness measurements. The nanohardness values for the three materials are in the order of 0.2 to 0.25 GPa. These measurements are within the hardness values obtained for composite resins for dental use, which according to studies are from 0.2 to 1.6 GPa [10, 45], while the hardness value of natural tooth enamel is 5.58 [46], and the values found for dentine are between 0.5 and 1.3 GPa. This last value depends on the distance from the center of a dentinal tubule to the place where the measurement is taken, being greater where this distance is lower [47].

Figure 9 shows the results of the nanohardness analysis. Statistical analysis using the Tukey HSD test indicates that there is no significant statistical difference between the samples ($p < 0.05$). This may be due to the fact that all materials have same filler concentration, and literature postulates that hardness depends on the quantity of filler [9, 10, 14, 25]. However, other studies postulate that the hardness and other tribological properties are determined not only by the quantity of filler but also by the type and quantity of silanizing agent, as well as the method of surface modification of the filler [17, 48]. This may be responsible for the fact that the lowest average hardness value was obtained with materials containing zirconia which was not functionalized (0.22 ± 0.02 GPa vs nanoparticles $= 0.24 \pm 0.01$ GPa and silica nanoclusters $= 0.25 \pm 0.04$ GPa).

Some studies report that particle size affects hardness, and that microparticles have improved hardness at relatively higher concentrations than nanoparticles, while dental composites reinforced with nanoparticles display high hardness values [18]. The results of this investigation show no effects on hardness either on the part of particle size, or based on the use of nonaggregate nanoparticles. In this case, the filler concentration was the determinant variable related to hardness.

4. Conclusions

Statistical analysis using the Tukey HSD test indicates that the samples with silica nanoparticles are statistically different to those that contain nanoclusters ($p < 0.05$). The roughness values obtained with silica nanoparticles were lower (22.6 ± 6.6 nm) than those obtained with silica and silica-zirconia nanoclusters (138.1 ± 36.6 nm and 116.2 ± 32.2 nm, resp.). Therefore, our hypothesis that lower roughness is obtained with nonaggregate silica nanoparticles was confirmed. Based on this investigation, it can be established that particle size is a determining factor in the roughness of the final material, supporting what has been stated in some studies in the literature, and redressing the lack of clinical data supporting this statement [34], as the methodology used allowed the use
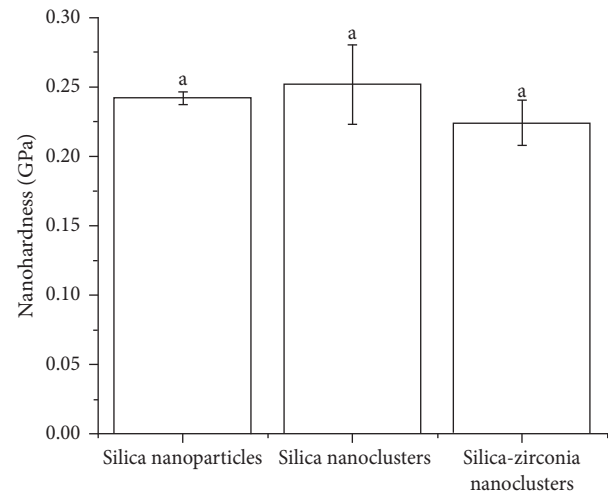

FIGURE 9: Nanohardness of materials reinforced with 30% by weight of particles. The letters indicate statistically homogenous groups (Tukey HSD test ($p > 0.05$)).

of different types of particles to be compared. However, in this regard, it should be taken into account that there are other variables that affect roughness, such as the bond strength between the particles that make up the nanoclusters, an aspect to consider when seeking to improve the performance of this kind of reinforcement materials.

With regard to nanohardness, according to Tukey statistical analysis, there are no significant statistical differences between the composite materials analyzed ($p > 0.05$). Therefore, our hypothesis that hardness is similar using nonaggregate nanoparticles and nanoclusters was confirmed (nanoparticles $= 0.24 \pm 0.01$ GPa, silica nanoclusters $= 0.25 \pm 0.04$ GPa, and silica-zirconia nanoclusters $= 0.22 \pm 0.02$ GPa). Although nanohardness can be influenced by variables such as functionalization and particle size, the results of this study show that nanohardness was determined by the concentration of the reinforcement materials.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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