

Article

Effect of the Silanization of Aerosil OX50 in the Properties of Light-Cured Dental Composites

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Abstract: In this study, the surface of aerosil OX50 was treated with γ -methacryloxypropyltrimethoxysilane in order to evaluate its effect on light-cured dental composites. Four composites were prepared with Bis-GMA/tetraethylene glycol dimethacrylate/ γ -methacryloxypropyltrimethoxysilane, Bis-GMA/tetraethylene glycol dimethacrylate, and a 45% treated or untreated aerosil OX50, using the camphorquinone/*N,N*-dimethylaminoethyl methacrylate pair as initiator. Evidence of filler silanization was provided by FTIR as a low-intensity absorption at 1707 cm^{-1} (carbonyl functional group) while thermogravimetric analysis showed a mass loss of approximately 2% associated with the decomposition of γ -methacryloxypropyltrimethoxysilane. The experimental composites studied meet the requirements of the ISO 4049:2019 standard for depth of cure, water sorption, and solubility. The composites are shown to be thermally stable and presented a degree of conversion higher than 70%, being higher than that reported for many commercial composites. Based on the observed properties, the best formulations were those in which the silane is incorporated into the matrix and the filler was previously treated.

Keywords: aerosil OX50; light-cured dental composites; silanization



Citation: Díaz-Rodríguez, S.d.l.C.; Tarano-Artigas, O.; Herrera-Kao, W.; Cauich-Rodríguez, J.V.; Cervantes-Uc, J.M.; Rosa-Sainz, A.; La Serna, A.A.; Veranes-Pantoja, Y. Effect of the Silanization of Aerosil OX50 in the Properties of Light-Cured Dental Composites. *Appl. Sci.* **2024**, *14*, 2453. <https://doi.org/10.3390/app14062453>

Academic Editor: Vittorio Checchi

Received: 28 January 2024

Revised: 7 March 2024

Accepted: 12 March 2024

Published: 14 March 2024



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1. Introduction

Dental caries is one of the most widespread diseases in humanity, and it is defined as an infectious, multifactorial, chronic, and localized disease that affects the hard tissues of the tooth. It is produced by the action of organic acids from microbial fermentation of carbohydrates in the diet, the characteristics of the dental tissue, and the hygiene of each individual [1]. For a long time, the most widely used restorative material in the repair of dental tissue has been silver amalgam. Its adequate physical–mechanical properties and ease of handling have made it the ideal material for the restoration of posterior teeth. However, it presents drawbacks such as its unnatural appearance, the lack of adhesion to dental tissue that generates more sacrifice of healthy dental tissue, and the contamination produced by mercury [2]. For this reason, some countries prohibit the use of amalgam, and work is underway worldwide on the gradual reduction of the use of compounds that contain mercury, which is declared in the Minamata Convention, and its total elimination is proposed for the year 2030 [3,4].

The appearance in restorative dentistry of light-cured composite resins has been one of the most significant contributions as it considers the preservation of healthy tissue,

reduction of microleakage, and prevention of postoperative sensitivity. In general, composite resins or dental composites are made up of a mixture of acrylic monomers made up of an organic matrix, filler particles, a coupling agent, whose function is to achieve an optimal bond between both components, and an initiator system [5]. The organic matrix of dental composite resins is basically made up of two types of monomers that are divided according to their viscosity into base monomers and diluents. 2,2 [p-(2-hydroxy-3-methacryloxypropoxy) phenyl] propane (Bis-GMA) is the most commonly used base monomer for this purpose due to its properties such as low shrinkage upon polymerization, rigidity, and high resistance [6]. However, it has a high viscosity that negatively affects the final properties of the composite, requiring the use of diluent monomers such as tri- and tetraethylene glycol dimethacrylates (TEGDMA and TEEGDMA, respectively) [7]. Quartz, glass, titanium oxide, and silicon oxide are generally used as inorganic fillers, providing an increase in the resistance to traction, compression, and abrasion of composites. Hydroxyapatite could be a promising bioactive filler for dental resin composites, since it is the main biological component of dentin and enamel [8,9]. In addition to reducing shrinkage in composites it is desirable that mechanical properties are like that of the dental structure in order to guarantee a restoration that meets physical, chemical, and mechanical needs, i.e., an aesthetic and biocompatible dental composite. Currently, there is a trend to use nanofillers to obtain composite resins with dental applications, since these improve the wear properties of the composites, such is the case of aerosil OX50. This is a fumed silica made up of spherical particles of 40 nm in diameter. This silica is obtained by flame hydrolysis of silicon tetrachloride, SiCl_4 [10,11].

Among the most important properties of dental resins for clinical use are the degree of conversion, water sorption and solubility, and the mechanical properties. The values required for these properties are well known and have been established in various international standards [12]. The degree of conversion of the composites expresses the number of double bonds of the methacrylate monomeric groups that react. It can be determined by infrared spectroscopy, considering the decrease in the intensity of the absorption band of the double bonds corresponding to the aliphatic carbons [9]. The depth of cure is also a property that indicates the effectiveness of the polymerization process and is carried out according to the established parameters in the ISO 4049 standard [12,13]. Other properties that are evaluated and regulated (ISO 4049) are water sorption and solubility. The latter is of great importance since these materials will be placed in a humid environment where unreacted monomers may dissolve or the filler particles can be leached into the oral environment, affecting its clinical behavior and its biocompatibility [14].

Obtaining good properties in composite resins depends largely on the bond between the matrix and the filler. With a good bond, the detachment of inorganic particles is avoided, as well as the penetration of water in the interface, and then the deterioration of the restoration. To ensure the formation of a proper interphase, the filler is treated with coupling agents, generally silanes. The most widely used silane is γ -methacryloxypropyltrimethoxysilane (MPS), capable of chemically interacting with both the matrix and the surface of the filler [15,16].

In the 1970s, "two-step" silanization methods were developed, either by dry contact or in solution, which involve a pretreatment of the filler with the silane before its incorporation into the monomeric mixture for the formulation of composite resins. Other methods that have been used include the "one-step" treatment, which consists of incorporating the silane directly into the organic matrix [17]. Several types of aerosil have been used as previously reported and MPS silanized aerosil with smaller particle size rendered better adhesion with a Bis-GMA matrix but the amount of sorbed water increased. However, the use of larger particle sizes (40 nm) like aerosil OX50 did not severely affect their mechanical performance as their bending strength is slightly lowered without sacrificing flexural modulus [17].

Recently, changes have been introduced in the composition of dental resins with the aim of improving their properties and in order to reduce the use of bisphenol A, where the main concern is the possible release of monomers [5]. In addition to these alternative

monomers, the use of monomers with antibacterial activity has also been pursued but the most significant enhancements and changes have been in fillers such as size reduction and shape enhancement (plate-like, rod-like, nanoparticles) [18].

In this research, MPS is introduced into organic matrices not only as a partial diluent of Bis-GMA (Bis-GMA/TEGDMA/MPS) but also as a coupling agent. Therefore, the aim of this study was to evaluate the influence of the surface treatment of aerosil OX50, used as an inorganic filler, on various properties of dental composites including degree of conversion, depth of cure, water sorption, and solubility.

2. Materials and Methods

In this section, the materials and methods used are presented. The section is subdivided into: silanization of aerosil OX50, preparation of dental composite formulations, and characterization of the filler and experimental composites.

2.1. Silanization of Aerosil OX50

To improve the surface adhesion between the organic matrix and inorganic particles, the filler was treated with MPS (Sigma Aldrich, Burlington, MA, USA). The silanizing solution was prepared with 80 mL of acetone, 0.5 mL of H₂O, 1 mL of MPS, stirred for 20 min, and then 1 g of aerosil OX50 (DEGUSSA, Tokyo, Japan) was added. Silanization in acetone/water mixtures was conducted as in previous studies that demonstrated a better incorporation of silicon on hydroxapatite surfaces in comparison to the use of methanol/water mixtures [19]. Magnetic stirring was continued for 2 h. Subsequently, it was placed in an ultrasonic bath for 20 min and stirred again for 2 h with a magnetic stirrer. It was decanted and washed with sufficient acetone. The treated aerosil OX50 was dried for 12 h in an oven at 60 °C. Figure 1 shows the schematic diagram of the procedure performed to obtain the silanized aerosil OX50.

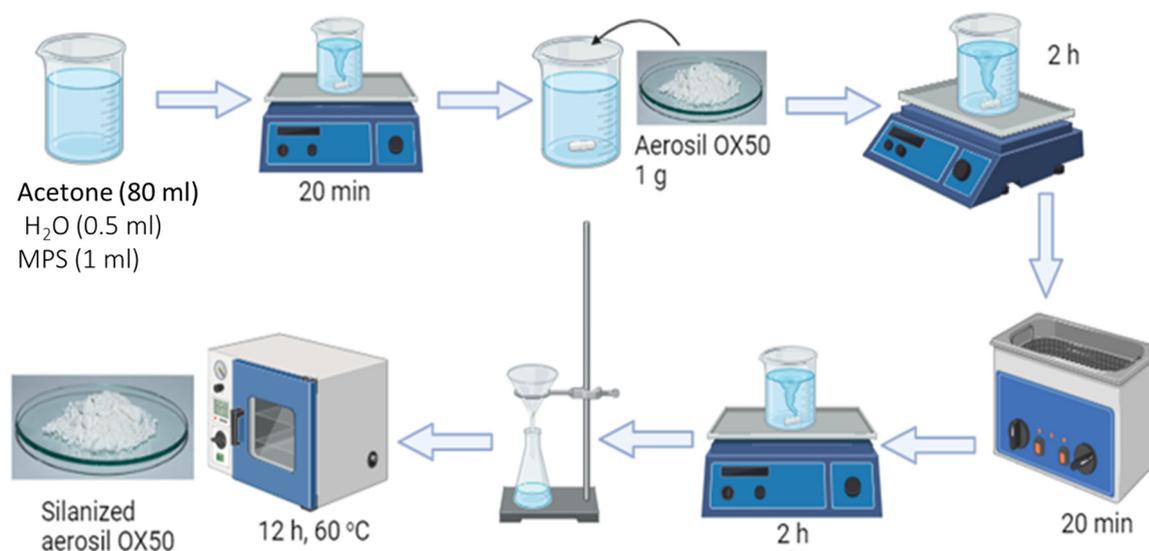


Figure 1. Scheme of the silanization process.

2.2. Preparation of Dental Composite Formulations

Four experimental light-cured dental composites were prepared with two different monomeric matrices and 45% aerosil OX50 as an inorganic filler (Table 1). The M1 matrix is made up of Bis-GMA/TEGDMA/MPS (60:30:10) and the M4 matrix is made up of Bis-GMA/TEGDMA (60:40). All composites contain Bis-GMA from Sigma Aldrich, USA, in their organic matrix while tetraethylene glycol dimethacrylate (TEGDMA) was purchased from Fluka. The C145 composite has MPS incorporated into its organic matrix as part of the diluent, while C445 does not. In addition, the C145s and C445s composites contain

filler previously silanized with MPS. The camphorquinone (CQ, Aldrich, USA)/N,N-dimethylaminoethyl methacrylate (MDMAE, Riedel de Haen, Seelze, Germany) pair was used as the initiator system. As reference material, the commercial Tetric Evo Ceram[®] (TT) was used. All the reagents used were 98% pure.

Table 1. Composition of experimental light-cured dental composites.

Composites	Organic Matrix	Inorganic Filler
C145 C445	Bis-GMA/TEEGDMA/MPS (M1) Bis-GMA/TEEGDMA (M4)	Aerosil OX50 (45%)
C145s C445s	Bis-GMA/TEEGDMA/MPS (M1) Bis-GMA/TEEGDMA (M4)	Aerosil OX50 silanized (45%)
TT	Bis-GMA/TEGDMA	Mixtures of oxides and copolymers (82%)

The light source employed to cure the materials was a light-emitting diode (LED) from Woodpecker (Guilin, China) with a wavelength range from 420 to 480 nm and a light intensity of 1000 mW/cm².

2.3. Characterization of the Filler and Experimental Composites

To verify the occurrence of filler silanization and to analyze the thermal behavior of dental composites, a thermogravimetric analysis (TGA) of 50 to 800 °C was performed in a Perkin Elmer TGA-7 (Norwalk, CT, USA), with a heating rate of 10 °C/min and nitrogen flow of 50 mL/min. For the study, 3 mm diameter and 1 mm thickness samples were prepared after polymerization for 40 s.

The morphology of silanized and unsilanized aerosil OX50 was observed on a TESCAN VEGA3 scanning electron microscope, and it was coated using an ion sputter coater SBC-12 (KYKY TECHNOLOGY CO., Beijing, China). The study was carried out at an acceleration voltage of 25 kV with a magnification of 50,000 times. From the micrographs obtained, 100 measurements of aerosil OX50 particles were made using the ImageJ program, version 1.54d. These measurements allowed us to obtain particle size distribution of the filler and thus estimate their average size.

Fourier transform infrared spectroscopy (FTIR) was used for the characterization of the filler and determination of the degree of conversion in the composites. The aerosil OX50 was analyzed in a Thermo Nicolet 8700 spectrometer (Madison, WI, USA), with a resolution of 4 cm⁻¹, 100 scans, and in the spectral interval of 4000–500 cm⁻¹. The samples were dispersed in KBr and the degree of conversion (DC) determined by recording transmission spectra in the 4000–600 cm⁻¹ range, with the same resolution and 50 scans. Three replicates of each sample were run at 0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, and 80 s after irradiation. The DC of every dental resin composite was calculated from the absorbance intensities (*R*) of the aliphatic C=C bond (1638 cm⁻¹) against the internal standard of the aromatic C=C bond (1608 cm⁻¹), determined before and after polymerization. The degree of conversion (%) was calculated according to Equation (1) [20–22].

$$DC (\%) = 100 \times [1 - (R_{cured} / R_{not\ cured})] \quad (1)$$

The depth of cure, water sorption (*A*), and solubility (*S*) tests were evaluated according to the specifications described in the ISO 4049:2019 standard [12]. For the depth of cure, three cylindrical specimens (6 mm in height and 4 mm in diameter) were irradiated for 40 s on one side. After the polymerization process, the specimen was removed from the mold and any soft material was scraped using a plastic spatula. The height was measured with a micrometer (0–25 mm, 0.01 mm precision), the obtained value was divided by two, and the measured magnitude was reported as the depth of cure of the material. Water sorption and solubility tests were performed using five disc-shaped specimens (1 mm in

height and 15 mm in diameter). The samples were cured with nine overlapped irradiations on one side (40 s for each irradiation; 360 s in total). Diameter and thickness are measured with a micrometer (0–25 mm) to calculate the volume (V). The samples are weighed and stored in a desiccator until constant weight, the final mass is taken as m_1 . Then, they are immersed in distilled water (m_2) for seven days at 37 °C and placed again in a desiccator until a constant mass (m_3). For the calculations, Equations (2) and (3) were used.

$$A = (m_2 - m_3)/V \quad (2)$$

$$S = (m_1 - m_3)/V \quad (3)$$

The Origin8 computer program was used for data processing. Statistical analysis was performed by comparing means and variances with the Statgraphics Plus 5.5 program, using Student's "t" statistic and Fisher's "F" statistic with 95% confidence. The mean and standard deviation (Sd), as an interval (\pm), were reported for all cases.

3. Results

This section presents the obtained results, which are divided into: characterization of the filler, physical appearance of the experimental composites, and characterization of the experimental composites.

3.1. Characterization of the Filler

FTIR spectra, mass loss (TGA), and the first derivative (DTGA) of the silanized and untreated aerosil OX50 are shown in Figure 2a,b. The FTIR spectrum of non-silanized aerosil OX50 showed two typical bands of silicon oxide at 1100 and 801 cm^{-1} . In the case of silanized aerosil OX50, an almost imperceptible third band can be observed around 1707 cm^{-1} . In the TGA of the untreated aerosil OX50 no mass loss was observed, which can be explained by the high stability of SiO_2 . In contrast, silanized aerosil OX50 showed a decomposition temperature at 437 °C with a mass loss of approximately 2%.

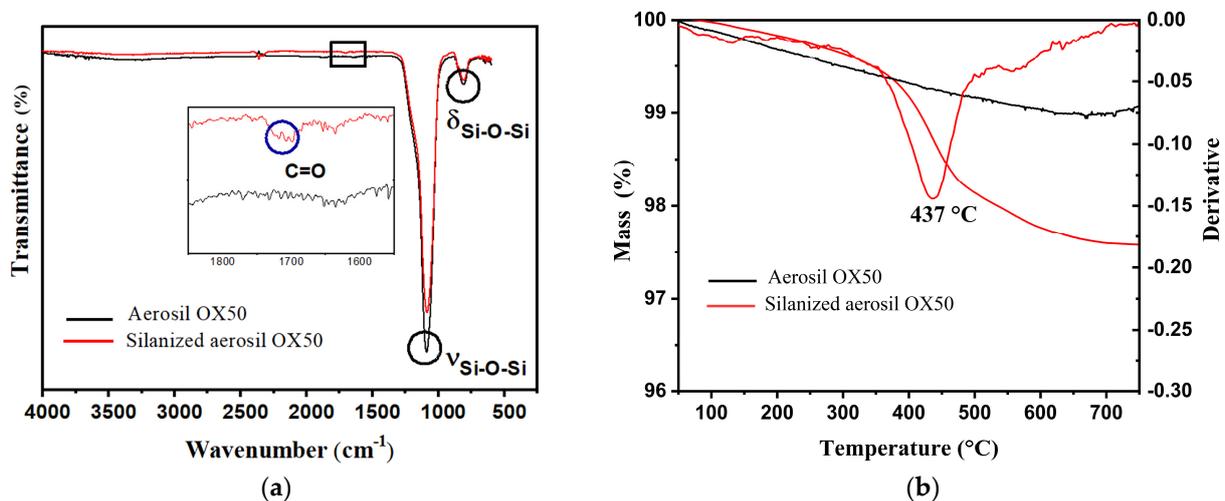


Figure 2. Characterization of the filler: (a) FTIR spectrum; (b) TGA thermograms of untreated and silanized aerosil OX50.

Several micrographs of aerosil OX50 were taken before and after silanization and representative ones are shown in Figure 3. In general, aerosil OX50 particles are spherical in shape and easily agglomerate, which is typical of nanoparticles. The agglomerates in the untreated aerosil OX50 (Figure 3a) are round and 150 nm in size. In the case of the silanized aerosil OX50 (Figure 3b), there is an increase in the cohesion between the agglomerated particles.

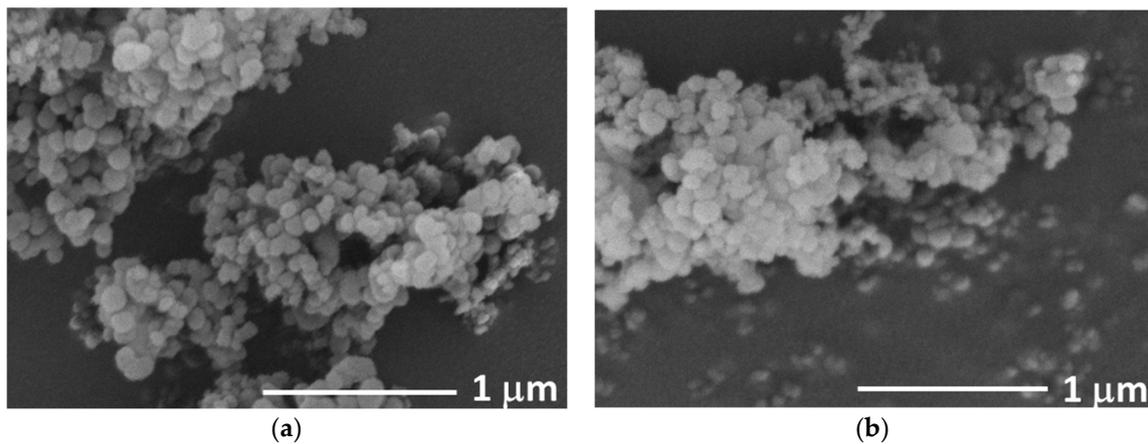


Figure 3. Characterization of the filler: (a) micrograph of unsilanized aerosil OX50; (b) micrograph of silanized aerosil OX50.

The particle size distribution of aerosil OX50 (Figure 4), obtained from micrograph measurements, shows a normal distribution. Most of the particles are in the 40–50 nm range in agreement with the manufacturer’s description. Furthermore, no polydispersity is observed, and the average particle size was 44 ± 1 nm.

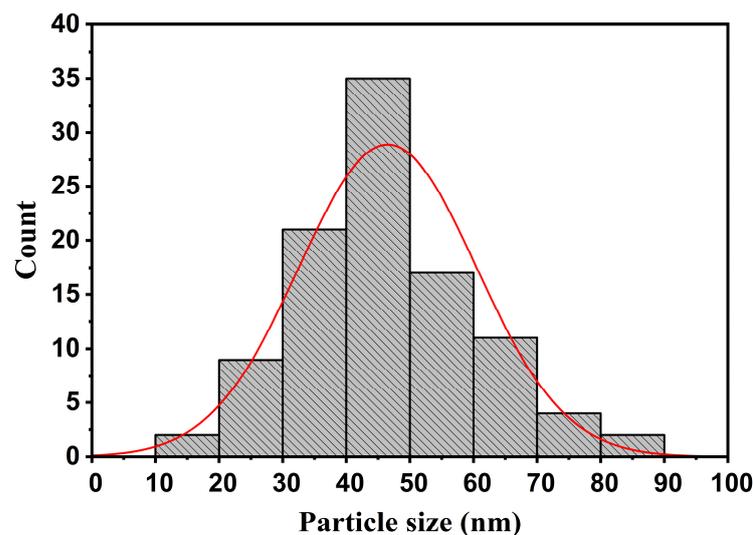


Figure 4. Particle size distribution of aerosil OX50.

3.2. Physical Appearance of the Experimental Composites

The four experimental composites, prepared with the monomeric matrices M1 (Bis-GMA/TEEGDMA/MPS) and M4 (Bis-GMA/TEEGDMA) and 45% aerosil OX50, are homogeneous pastes, easy to handle, and of similar consistency and color to commercial resins. The most viscous composites, as visually appraised and the most difficult to manipulate, are those that contain the M4 matrix, because the diluent monomer (TEEGDMA) is more viscous than the TEEGDMA/MPS mixture. In addition, in composites prepared with the Bis-GMA/TEEGDMA/MPS matrix, the filler is better incorporated. The commercial resin is a homogeneous, cream-colored paste, slightly more viscous than that prepared with the Bis-GMA/TEEGDMA matrix. The monomeric mixtures have a similar color (yellow) due to the presence of camphorquinone, with a color change after polymerization.

3.3. Characterization of the Experimental Composites

The measurement of the degree of conversion of the unsilanized and silanized experimental composites and the monomeric mixtures was carried out at 0, 1, 2, 3, 4, 5, 10, 15,

20, 25, 30, 35, 40, and 80 s of irradiation. Figure 5a shows the FTIR spectrum of the C145 composite at the different irradiation times mentioned above. The curves corresponding to each time are indicated in different colors from blue for time 0 to red for 80 s. The two bands under study in this research can be observed in the spectrum. The band corresponding to the aliphatic C=C bond appears around 1637 cm^{-1} , while the one associated with the vibrations of the C=C aromatic bond can be seen around 1612 cm^{-1} . Figure 5b shows the results obtained from the determination of the degree of conversion with time. Generally, only the degree of conversion at the final irradiation time, which in normally 40 s, is reported. In this study, in addition, the results of the degree of conversion at several times up to 80 s are reported and analyzed.

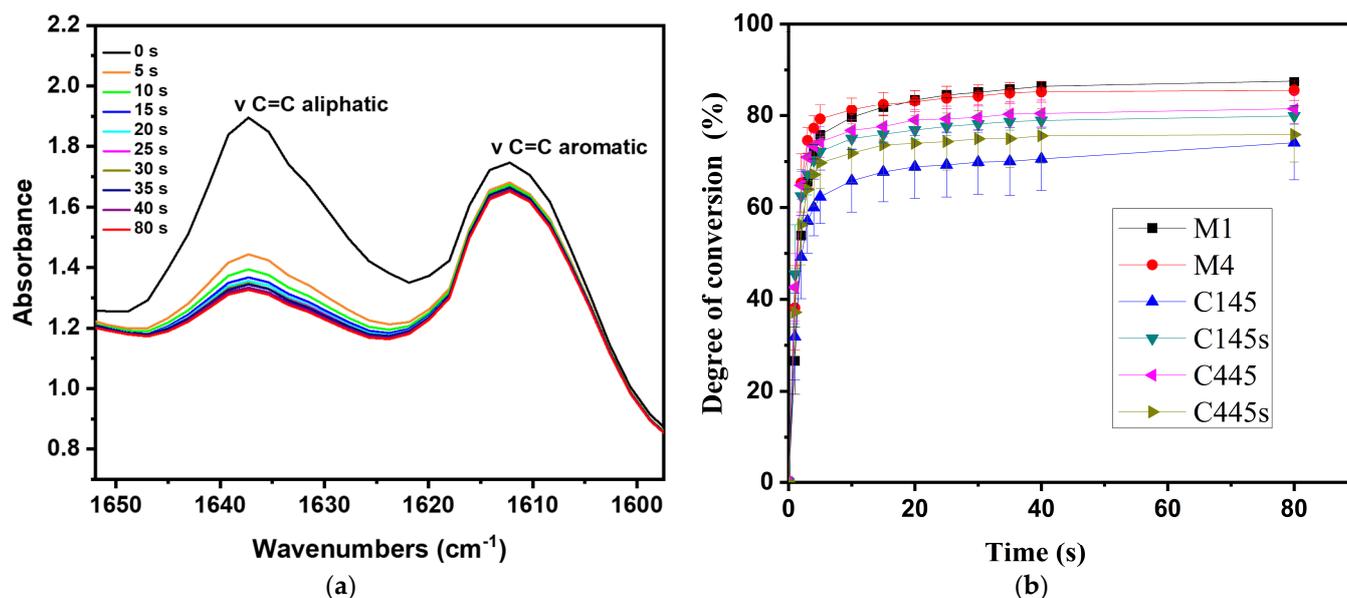


Figure 5. (a) FTIR spectrum of the C145 composite in the region from $1680\text{--}1580\text{ cm}^{-1}$ at different irradiation times; (b) Degree of conversion vs. irradiation time of the matrices and composites.

The results of the depth of cure and degree of conversion at 40 s for the matrices and composites are shown in Table 2. Composite materials meet the requirements of the ISO 4049:2019 standard [12] for cure depth, showing values greater than 2 mm. The highest values are exhibited by the monomeric matrices M1 and M4, (2.95 ± 0.01) mm and (2.94 ± 0.01) mm, respectively. In addition, there are no statistically significant differences between the monomeric matrices M1 and M4, nor between the composites prepared with them, so no effect of the silanization process was observed for this property. The experimental composites showed a greater value of curing depth than the commercial TT composite used as a reference.

Table 2. Degree of conversion at 40 s and depth of cure.

Samples	DC (%)	Depth of Cure (mm)
Property Value	55–80	≥ 2
M1	86.3 (0.1) ^a	2.95 (0.01) ^a
M4	85 (2) ^{a,b}	2.94 (0.01) ^{a,b}
C145	71 (5) ^c	2.93 (0.02) ^b
C145s	79 (2) ^d	2.93 (0.01) ^b
C445	80 (3) ^{b,d}	2.93 (0.01) ^{a,b}
C445s	76 (6) ^{c,d}	2.93 (0.02) ^{a,b}
TT	63 (4) ^e	2.67 (0.09) ^c

^{a,b,c,d,e} Statistically homogeneous groups (analysis by properties).

In the case of the degree of conversion for the matrices and composites at 40 s of irradiation, values higher than 67% and, in several cases, more than 75% (C145s and C445) were obtained. As shown in Table 2, all experimental composites present DC values higher than TT, except for composite C145, which does not have significant differences from it. Furthermore, the highest values of this property correspond to matrices M1 and M4, ($86.3 \pm 0.1\%$) and ($85 \pm 2\%$), respectively.

The results of the water sorption and solubility test are shown in Figure 6. The highest values of this property evaluated for the different formulations correspond to the pristine monomeric matrices M1 and M4, which slightly exceed the limit value in the ISO 4049:2019 standard [12]. In the case of absorption, the best values correspond to the C145s, C445 and C445s composites, and no significant differences between them are observed. Furthermore, the commercial TT composite showed the lowest water sorption values and significant differences with respect to the experimental composites. Regarding water solubility, no significant differences were observed between C145 and C145s, nor between C445 and C445s.

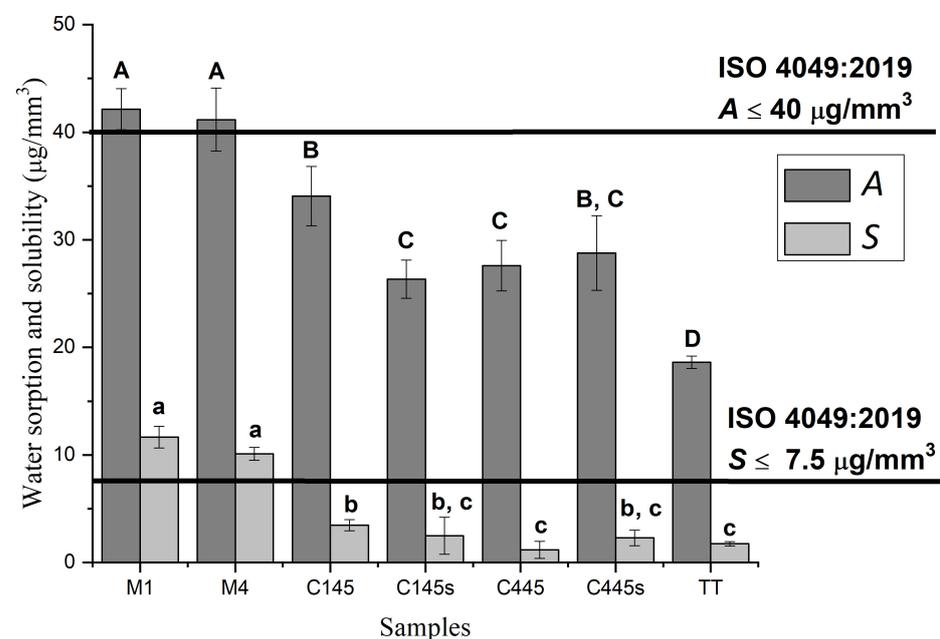


Figure 6. Water sorption and solubility for the matrices and composites. A, B, C, D and a, b, c are the statistically homogeneous groups for absorption and solubility, respectively.

The thermal degradation of dental composites and matrices can be visualized from the thermograms shown in Figure 7. As observed in Figure 7a, M1 and M4 have highest mass loss (90% at 700 °C and 89% at 500 °C, respectively) with respect to the other samples. In the case of composites, the greatest mass loss corresponds to the commercial TT (24.40%), followed by C145 (47.08%), C145s (49.00%), C445 (49.36%), and C445s (55.68%). The analysis of the first derivative (Figure 7b) indicates that the degradation of the tested materials occurs in an interval of 250–650 °C. In addition, the matrices present two decomposition temperatures (M1: 400, 424 °C; M4: 408, 432 °C), and the C145, C145s, and C445 composites experience a single decomposition at 430, 424, and 420 °C, respectively. The commercial composite experiences two endothermic effects, one at 368 °C and the other at 451 °C. On the other hand, the C445s composite experiences three endothermic effects (372, 420, and 600 °C).

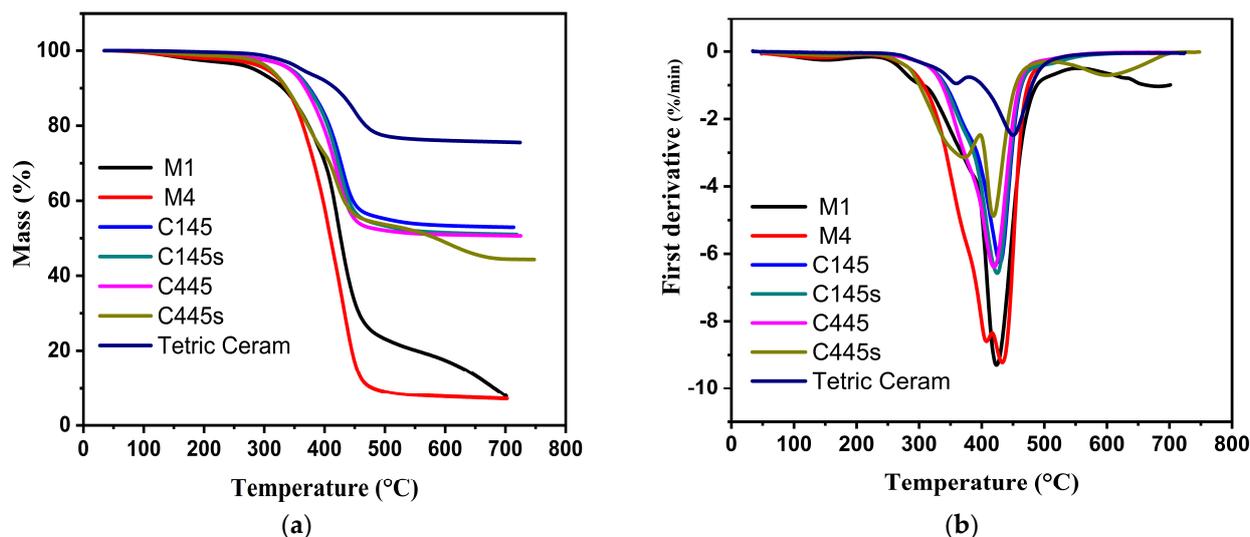


Figure 7. (a) Thermogravimetric curves; (b) First derivative of the thermogravimetric curves of matrices and composites.

4. Discussion

Silicon dioxide presents three characteristic absorption bands at 1080 , 800 , and 450 cm^{-1} , which correspond to the vibration modes of stretching, bending, and rocking of the Si-O-Si bonds, respectively. In the IR spectra of the untreated and silanized aerosil OX50 (Figure 2a) only two of the characteristic bands of silicon dioxide are observed, since the spectrum was recorded between 4500 and 650 cm^{-1} . The highest-intensity band appears around 1100 cm^{-1} and the least intense one at approximately 801 cm^{-1} , corresponding to the stretching and bending vibrations of the Si-O-Si bonds, respectively. The authors have verified the occurrence of silanization by the presence of a band of low intensity around 1707 cm^{-1} in the spectrum of silanized aerosil OX50 (Figure 2a), corresponding to the vibrations of the carbonyl group present in the MPS coupling agent [23]. The low intensity of this band suggests that a very small percentage of silane is incorporated, making it almost imperceptible for this characterization technique.

When the TGA curves of the unsilanized aerosil OX50 (Figure 2b) are analyzed, it is observed that the mass of the sample remains practically constant, which is due to the thermal stability of silicon dioxide. In the case of the treated aerosil OX50, the loss of 2% mass is associated with the decomposition of the MPS. In this sense, it has been reported that the physical decomposition of silane physically absorbed on the surface occurs between 50 and 150 °C , while the silane chemically bonded to the filler decomposes between 200 and 600 °C [24]. These results demonstrate the appearance of the silanization process of the filler.

The authors report that nanoparticle resins are highly aesthetic and their physical and mechanical properties are superior to others, presenting less contraction during polymerization and high resistance to fracture, compression, and traction [25]. With a smaller particle size, a better finish of the restoration is achieved, which is observed in its surface texture, reducing the possibilities of biodegradation of the material. In addition, this technology has allowed the mechanical properties of the resin to be suitable for both the anterior and posterior sectors [26]. In the micrographs of aerosil OX50 (Figure 3) it can be seen that it is formed by spherical particles in agreement with Aminoroaya et al. [8], suggesting that dental composites containing smaller spherical silica particles result in more uniform stress distribution and a reduction of stress at the filler–matrix interface. An increase in filler size is expected to increase the stress concentration at the filler–matrix interface, causing more susceptibility to crack nucleation in this area due to the different rigidities of organic matrix and inorganic filler, leading to lower mechanical performance, such as lower strength of the dental composites.

According to the manufacturer's technical indications [27], aerosil OX50 is a hydrophilic fumed silica and its average particle size is 40 nm. The slight increases in the quantity and size of the agglomerates observed for the silanized aerosil OX50 (Figure 3b), as well as the small irregularities generated, have no influence on the morphology of the particles. Despite these differences in the agglomerates, it is considered that the silanization process does not alter the particle morphology. These results coincide with those obtained by other authors who suggest that the presence of the silane molecule covalently bound to the silicon oxide implies new interactions between the nanoparticles and, therefore, a new arrangement of the aggregates. One way to explain this change is that the appropriate modification of the surface of a nanoparticle by a silane coupling agent involves the removal of the hydroxyl groups present on its surface together with the formation of new siloxane bonds (-Si-O-Si) between them. This new interaction causes the alteration in the agglomerates of the nanoparticles before and after the silanization process. In addition, during the development of this process, the first reaction that occurs is the hydrolysis of the alkoxy groups of the silane molecule that become silanol groups (-Si-OH) and, when this occurs, the silane molecules can react with each other and form dimers or oligomers.

Light-cured composite resins have the advantage of being systems with unlimited working time before the material cures. However, the efficiency in polymerization is of prime importance in their behavior. The degree of conversion indicates the percentage of double bonds that have been converted into single bonds, that is, the number of monomers in the resin that have reacted to form polymers and can be determined by FTIR. In Figure 5a, it can be seen how the band corresponding to the vibrations of the aliphatic C=C double bonds decreases in intensity as the irradiation time increases, which demonstrates the progress of the polymerization process. Properties such as compressive and diametric compression strength, elastic modulus, as well as color stability, solubility, and cytotoxicity, are closely related to the conversion. A low degree of conversion favors the presence of residual monomer inside the cavity, which can be toxic to the pulp, demonstrating that this property is closely related to the biocompatibility of composite resins. For these materials, the conversion from monomer to polymer occurs from 55–75% [28]. The nature of the monomers that make up the monomeric matrix, the filler content, the intensity of the irradiated light, and the irradiation time are aspects of great influence on this property. As can be seen in Figure 5b, in all cases there is a sudden increase in the degree of conversion early in irradiation. Then, this increase becomes less pronounced until 5 s of polymerization, from which time until 80 s the value of the property does not change appreciably, a factor that is due to the decrease in active centers (free radicals) and to their low mobility when the viscosity increases with the occurrence of the polymerization reaction.

The results obtained for the degree of conversion (Table 2) are totally satisfactory, as they give a measure of the lower toxicity that they can present if we compare them with the commercial composites in the literature. The higher DC values in matrices M1 and M4 are because the monomeric mixtures do not contain filler. It is known that the inorganic filler influences this property, since it increases the viscosity of the composite and hinders the diffusion of light emitted during irradiation and in some cases also the mobility of the organic molecules. The composites obtained have a degree of conversion between 65% and 85%, which is higher than those reported in other studies, as in the case of Nor Ain Fatihah Azlisham et al. in 2023 [29]. They evaluated the degree of conversion of different dental resins containing nanohybrid silica derived from rice husk as inorganic filler (40, 50, and 60% by weight). For these composites, they obtained conversion values from 60–65%.

The result of the statistical test for the degree of conversion shows that there are significant differences between the formulated materials. To determine which composite materials present significant differences among themselves, a multiple comparison test was performed. This showed that there are no significant differences between the degree of conversion of the Bis-GMA/TEEGDMA/MPS (M1) and Bis-GMA/TEEGDMA (M4) monomeric matrices and between the composites prepared with M4 (C445 and C445s). In the case of composites prepared with the monomeric matrix containing MPS (M1), there

are significant differences between C145 and C145s and the highest value of the property corresponds to the C145s composite.

The depth of cure is one of the standard properties that should be evaluated in light-cured composite resins and is an indirect measure of the polymerization efficiency, which is decisive in the behavior of composites. Uncured material can migrate into the oral environment and cause allergic reactions in some patients, as well as stimulate the growth of bacteria around the restoration [30]. The ISO 4049:2019 standard [12] requires that these materials have a curing depth greater than 1.5 mm and that the loss of uncured material must be less than 0.5 mm, that is, that the optimal curing depth is equal to or greater than 2 mm. The maximum value recommended to dentists to layer composites when performing restorations in deep cavities is 2 mm. As can be seen in Table 2, the highest values correspond to the monomeric matrices M1 and M4, (2.95 ± 0.01) and (2.94 ± 0.01) mm, respectively. One of the factors that explains the high depth of cure values for the monomeric mixtures is the structure of the monomers used in the preparation of the mixtures (Bis-GMA, TEEGDMA), which polymerize by the two existing methacrylate groups at their ends. Thus, a higher degree of cross-linking is achieved with a lower amount of residual double bonds, which produces a higher efficiency in polymerization.

It has been reported that with thiourethane-functionalized fillers, it is possible to improve the properties of dental resins, such as the curing depth. This was attributed to the increase in refractive index provided by the presence of thiol, thiocarbamate, and aromatic groups, which minimizes the mismatch with the refractive index of the filler during polymerization and improves light penetration at depth [21].

Water sorption and solubility are parameters that must be controlled in dental materials. Both are related to the amounts of unreacted monomers and other non-polymerizable molecules, as well as to some small polymer chains that can migrate from the cure matrix into the medium. The sorption in the oral cavity can reduce the physical and mechanical properties of composites. This reduction is mainly attributed to the hydrolytic rupture of the bond between the filler and silane, which created a fissure. The sorption is then considered as a measure of the structural changes in the polymeric matrix, and the solubility is considered as an indirect measure of the toxicity of the material. The ISO 4049:2019 standard [12] refers to adequate sorption values as those that are less than or equal to $40 \mu\text{g}/\text{mm}^3$ and solubility values that are less than or equal to $7.5 \mu\text{g}/\text{mm}^3$. The highest values of these properties correspond to the monomeric matrices and slightly exceed the limit reported in the standard. In this sense, it is known that the Bis-GMA, TEEGDMA, and MPS monomers present in the organic matrix have oxygen atoms that, when interacting with the protic solvent, form hydrogen bonds with it, favoring water sorption. The statistical analysis and the subsequent multiple comparison test developed with the water sorption values showed significant differences between the C145 and C145s composites, the latter being the one with the lowest value. It should be remembered that the C145s composite is the one that contains MPS as part of the diluent and the silanized filler, a factor that contributed to the result, demonstrating the effectiveness of the treatment by both methods to improve the surface bond. No statistically significant differences were found between the monomeric matrices M1 and M4, nor between the C445 and C445s composites, so in this case there are no effects of the particle silanization on their solubility. These results are not in complete correspondence with those obtained for the depth of cure. Regarding the water solubility of the composites, the statistical analysis showed that there are no statistically significant differences between the composites prepared with the same matrix, so the surface treatment of the filler had no impact on this property. The results obtained for the C445 and C445s composites coincide with the results obtained for the degree of conversion.

Thermogravimetric tests allow the characterization of the thermal degradation processes that occur in different materials. In the case of the composites evaluated, the mass losses correspond to the relative composition of each of them and are associated with the degradation of the polymeric matrix that is part of the composites. Their degradation

occurs from 250 to 650 °C, a temperature that coincides with those reported in the literature for commercial composites [31]. The C445s composite presents three endothermic effects at 372, 420, and 600 °C corresponding to the gradual decomposition of the organic matrix. In this sense, it is known that the monomers that make up these organic matrices decompose, resulting in products such as methacrylic acid, 2-hydroxyethyl methacrylate, and phenolic compounds [23]. In the case of the commercial TT composite, the thermogravimetric test corroborated that the percentage of inorganic filler is around 76.60% and, according to what is reported in the literature, this value should be 80–82%. The difference between these values is due to the fact that the filler also contains copolymers that degrade during heat treatment.

It is important to remember that the maximum temperature that the oral environment supports when eating hot food is 50–60 °C [32,33]. Bearing this in mind, dental materials must have decomposition temperatures higher than those mentioned above, otherwise they would soften, causing restoration failure. We can then affirm that the composites obtained are thermally stable since their decomposition begins at 250 °C.

5. Conclusions

It was possible to demonstrate the appearance of the silanization process by FTIR and TGA, where in the case of the silanized aerosil OX50 a mass loss of around 2% is observed and associated with the decomposition of the MPS. On the other hand, the composites presented a degree of conversion higher than 70%, which in many cases exceeds those reported in the literature. The characterization of the experimental composites showed that they meet the requirements of the ISO 4049:2019 standard for depth of cure and water sorption and solubility. Thermal analysis showed that the studied composites are thermally stable, since the degradation of the matrix begins at 250 °C. The composites obtained have adequate properties that make them suitable for use as dental filler and, in addition, the prior silanization of the filler, together with the introduction of MPS as a diluent in the polymeric matrix, allowed greater compatibility between the organic matrix and the filler, which is manifested in the final properties of the C145s composite.

Author Contributions: Conceptualization and methodology, Y.V.-P., S.d.I.C.D.-R. and O.T.-A.; formal analysis, Y.V.-P., S.d.I.C.D.-R., O.T.-A., A.A.L.S., A.R.-S., J.V.C.-R., J.M.C.-U. and W.H.-K.; investigation, Y.V.-P., S.d.I.C.D.-R., O.T.-A., A.A.L.S., A.R.-S., J.V.C.-R., J.M.C.-U. and W.H.-K.; data curation, S.d.I.C.D.-R., O.T.-A. and Y.V.-P.; writing—original draft preparation, S.d.I.C.D.-R., O.T.-A. and Y.V.-P.; writing—review and editing, S.d.I.C.D.-R., O.T.-A., A.A.L.S., A.R.-S., J.V.C.-R., J.M.C.-U., W.H.-K. and Y.V.-P.; supervision, Y.V.-P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article.

Acknowledgments: Thanks to the Secretariat of Foreign Affairs (SRE) of the Mexican Embassy and the Mexican Agency for International Development Cooperation (AMEXCID) for the scholarship granted to one of the authors that allowed the characterization of the composite resins and the filler. The authors are grateful to J. García-Couce for her assistance in the review of the document and Nicolás Alberto Sirgado Pérez for his support in the morphological characterization of aerosil OX50.

Conflicts of Interest: The authors declare no conflicts of interest.

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