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Obtaining and characterizing dental hybrid composites with clay or silica nanoparticles and boron-aluminum-silicate glass microparticles

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Abstract

The aim of the present work was the obtaining and characterization of dental hybrid composites using nanoparticles (clay or silica) and boron-aluminum-silicate microparticles. We evaluated the dispersion of the nanofillers when changing their loading among 2.5%, 5%, 10% and 25% wt. Were tested, in the above quantities, four different types of nanofillers, two nanosilicas and two nanoclays. The remainder of the inorganic phase, up to a total loading of 75% wt, was given by the boron-aluminum-silicate microparticles. The systems were characterized by XRD, TGA, LF-NMR, and FTIR was used to determine the degree of conversion. The XRD and LF-NMR showed that the composites with 2.5% of clays, contained an exfoliated profile, and the groups with higher amounts of clay showed intercalated areas or the agglomeration of these particles. Furthermore, the silicas were agglomerated in all groups. The thermal resistance of the material was not affected by the silicas, but improved when using 2.5% of nanoclays. On the other hand, the addition of these particles caused the reduction of the degree of conversion of the systems.

Keywords: *acrylate matrixes, hybrid composites, organoclays, silicas.*

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1. Introduction

The quality of dental restorative composites have been steadily increasing in recent years^[1,2]. Dental composites usually consist of a polymer matrix with silanized filler and a photo-initiator system, with small amounts of photo-stabilizer and inhibitor, this composition represents a standard case of traditional design. The main monomers used in these materials are dimethacrylates, which include bisphenol A glycerolate dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA)^[1-3].

Adjustment of the filler amount and size is very important with respect to composition because this affects the overall properties of these materials. The field of nanotechnology involves materials in the 1-100 nm size range, should be it has brought new practices and including the use of many nanofillers^[4,5]. In dental composites, silica nanofillers, due to their high surface area and spherical form, cause a large increase in stiffness and decrease in roughness, however, the spherical and tiny shape leads to the formation of a high charge-charge interaction^[6,7], becoming more difficult to disperse than other fillers.

These materials require a high amounts of fillers for it to have a suitable viscosity to be sculpted. In this way the using of nanoparticles can cause difficulties of dispersion due to the high number of particles existing in a small mass

of fillers and due their higher surface energy^[8], encouraging the obtaining of hybrid composites with a combination of micro and nanoparticles. In resin composites is very common the use of glass particles with high atomic numbers, such as barium, strontium, and zirconium^[9].

Clay-polymer systems can have many morphologies, which include: (1) agglomerated particles, where the layers remain joined and polymer chains only interact with the surface layers; (2) intercalated, when the polymer chain is intercalated between the host platelets; and (3) exfoliated, when the silicate platelets are isotropically dispersed in a continuous polymer matrix. The best enhancements in physical properties can be achieved with the exfoliated topology^[10,11].

Montmorillonite is a 2:1 phyllosilicate. Its crystalline structure consists of an aluminum hydroxide octahedral sheet sandwiched between two tetrahedral silicate layers^[12]. Due to the organophilicity of the polymers, it is necessary to modify the clay surface with cationic surfactants such as alkylammonium or alkylphosphonium, forming the organoclay and providing expansion between the layers, facilitating the entry of the polymer chains within these. This is a key step to dispersion of these fillers in the polymer matrix^[11]. In this way, these materials are of great interest in composite resin research, due to their reduced dimension, which increases

the contact surface between matrix and fillers. In this field, nanoclay fillers are important and have been a subject of research in recent years due to the significant improvements small increments in these loadings can promote in the physicochemical properties of polymer composites^[13,14].

The aim of the present work was the obtaining and characterization of dental hybrid composites using montmorillonite clay and silica nanoparticles and boron-aluminum-silicate microparticles.

2. Materials and Methods

2.1 Materials

A standardized resin matrix was used containing a mixture of Bis-GMA, UDMA and TEGDMA in the proportion 35:40:25wt% between them, associated with a camphorquinone (CQ) system-based as photoinitiator. We used as the nanofillers one of the following four types: two organically modified clays (Viscogel® B8 and Dellite® 67G), a hydrophilic silica (Aerosil® 200) with 12 nm diameter, an organomodified silica (Aerosil® R972) with 16 nm diameter and a boron-aluminum-silicate glass with 4 µm diameter. In the case of both clay their lamellas present a diameter between 100 and 200 nm and 1 nm thickness. In the all groups, the total filler loading was 75% wt. The nanofiller-only loading varied among 2.5%, 5%, 10% and 25% wt, the remainder (72.5%, 70%, 65%, 50% wt, respectively) being the loading of microfillers.

All the mixtures were formulated to contain a standard loading of inorganic pigments based on metal oxide so that these experimental composites would match the A3 dentin color pattern on the Vita scale^[15]. In all preparations, the matrix used belonged to the same production batch, thus avoiding possible changes in composition. The clays and hydrophobic silica were surface modified, while the hydrophilic silica had no modification. Both clays have been modified by Bis(Hydrogenated Tallow Alkyl) Dimethyl Ammonium. But Dellite® 67G has high content of modifier, and Viscogel® B8 has 10% of 2-propanol. The hydrophobic silica, in turn, was modified by dimethyldichlorosilane (DDS). The surface modification of all fillers was made by the manufacturer.

The use of microparticles was necessary for the dental resins because these materials are worked at very high filler loadings due to the need for the resin to have high viscosity to enable modeling the restoration. This way, the presence of a mix with nano and microparticulated fillers in the dental resins led to obtaining hybrid composites.

2.2 Methods

The silicas and clay nanoparticles were combined with barium-alumino-silicate micrometer fillers glass (~4µm). The proportion of filler/matrix was 75:25 wt/wt. Within the nanofiller, the load percentages were 2.5%, 5%, 10% and 25% in relation to the microfillers. The matrix/filler proportion was similar in all groups, with the only change being the relative amount of microfillers and nanoparticles. The filler and matrix were mixed by a FlackTek DAC 150 SpeedMixer™ (Landrum, SC, USA), according to the following method: initially the nanofillers of each group were added to the matrix, after which the systems were

mixed in five cycles of five minutes each at increasing speeds of 1400, 1600, 2000, 2200 and 2400 rpm. Then, the microparticles were added to the mixture and subjected to the same mixing cycle, followed by two cycles of vacuum mixing (by manual rotation) for elimination of air bubbles that had been formed during mixing. The nanofillers were first added to the matrix in order to avoid high viscosity of the medium, which would hinder the dispersal of the particles.

X-ray diffraction

The exfoliation of nanoclay particles in resin and the crystallinity of silicas were analyzed by X-ray diffraction (XRD). The diffraction studies were performed with a Rigaku Ultima IV X-ray diffractometer (Tokyo, Japan) (CuKα irradiation, 40 kV, 20 mA) in the range of $2\theta = 1$ to 80° .

Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed on a Q50 thermobalance from TA Instruments, Inc. The samples with 15 mg were heated from 30 to 700°C , at a rate of $10^\circ\text{C}/\text{min}$, under nitrogen flow.

Degree of conversion

The degree of conversion (DC) of the systems was determined with Fourier transform infrared spectroscopy (FTIR: Spectrum 100 Optica; PerkinElmer, MA, USA), containing an attenuated total reflectance apparatus with a ZnSe crystal (Pike Technologies, Madison, WI, USA). The test was performed in the polymerized and unpolymerized samples and the DC was calculated using the band ratios of 1638 cm^{-1} and 1608 cm^{-1} . The analysis was performed in 5 different samples from each group evaluated ($N = 5$) in order to determine the statistical dispersions of the values.

Low-field nuclear magnetic resonance

To determine the relaxation measurements, a Maran Ultra low-field NMR (Resonance Instruments, Oxford, UK) was used, operating with the hydrogen nucleus at 23 MHz. Proton spin-lattice relaxation times were determined by inversion-recovery pulse sequence ($180^\circ - \tau - 90^\circ$) using 20 data points, with 4 scans for each and a range of τ varying from 0.1 to 5000 ms, with 10 s of recycle delay and 90° pulse of $4.5\text{ }\mu\text{s}$, calibrated automatically by the instrument's software.

3. Results

The silicas characterization using X-ray diffraction (Figure 1) revealed an unorganized structure characterized by the presence of an amorphous halo centered at $2\theta = 22.35^\circ$ for the hydrophobic silica (Aerosil® R972) and at $2\theta = 24.35^\circ$ for the hydrophilic silica (Aerosil® 200) presented two diffraction peaks. The broad diffraction peaks from silicas indicate the predominantly amorphous structure.

The diffractograms of the clays exhibit the characteristic peaks of montmorillonite structures. The peak d001 of both clays are very close to $2\theta = 2^\circ$ indicating their already high interlamellar spacing due to the presence of the surface modifier. In the clays' diffractograms (Figure 2), the basal spacing was determined by applying Bragg's equation: $n\lambda = 2 \sin \theta$ to d (001) peak. The calculations showed that

the basal spacing of the Dellite® 67G and Viscogel® B8 are 31.6 Å and 36.8 Å, respectively.

The composites diffractograms also revealed that the samples containing 5%-25% of both clays presented agglomerated systems because the peak d(001) stayed in a similar position as the pure clay. On the other hand in groups containing 2.5% of both clays, the d(001) peak disappeared, this result can reflecting the exfoliation of the clays in these systems, or even an increase in spacing between platelets greater than the limit of diffractometer detection (44 Å).

The initial degradation temperatures of all tested materials (Table 1) indicate that the silicas caused no significant changes in the thermal profile of the resins at any tested loadings, which may be related to the filler agglomeration. The clays, in turn, increased the thermal resistance of the material when used at 2.5% and reduced this resistance at the other loadings tested. This behavior indicates that the

less concentrated group presents better particle dispersion and the other clay loadings caused a more crowded profile.

From analysis of Low Field Nuclear Magnetic Resonance (LF-NMR), the longitudinal relaxation time of hydrogen (T₁H) values (Table 2) indicate that the Viscogel® 67G and Dellite® B8, when added to the system at a loading of 2.5%, caused a significant decrease in the spin-relaxation time of the hydrogen nucleus network, proving the formation of a composite with a high degree of exfoliation. The silicas, in turn, caused no significant change in the relaxation times compared with the control group (0% of nanofillers).

The results of DC obtained from the FTIR spectra (Table 3), showed that the degree of conversion of the evaluated resins comprised between 40.72% and 27.38%. As well it showed that the increase of nanoparticles in the system caused the reduction of the degree of conversion of these systems.

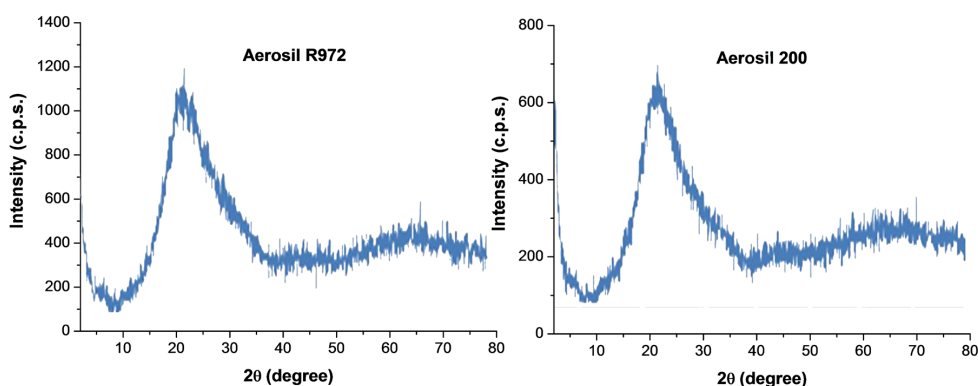


Figure 1. XRD patterns of (a) Aerosil® R972 and (b) Aerosil® 200.

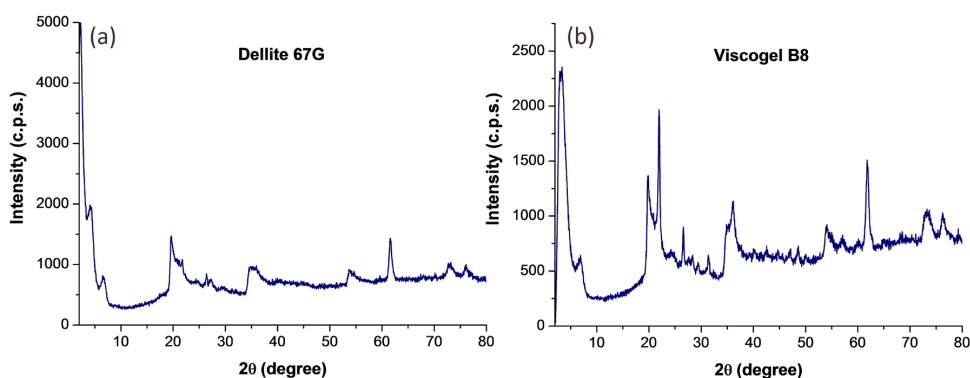


Figure 2. XRD patterns of nanoclays (a) Dellite® 67G (b) Viscogel® B8.

Table 1. Initial degradation temperatures of all tested materials.

Filler	Initial degradation temperature (°C)				
	0%	2.5%	5%	10%	25%
Dellite® 67G	369	379	351	333	332
Viscogel® B8	369	377	362	346	343
Aerosil® 200	369	369	364	369	367
Aerosil® R972	369	366	370	367	369

Table 2. T₁H values of all tested materials.

Filler	T ₁ H values (ms)				
	0%	2.5%	5%	10%	25%
Dellite® 67G	62	15	45	42	45
Viscogel® B8	62	15	42	46	54
Aerosil® 200	62	60	63	61	61
Aerosil® R972	62	59	59	62	60

Table 3. Degree of conversion of all tested materials.

Filler	Degree of Conversion				
	0%	2.5%	5%	10%	25%
Dellite® 67G	44 ± 3 A	38 ± 3 B	31 ± 2 C	29 ± 3 CD	28 ± 2 D
Viscogel® B8	44 ± 3 A	41 ± 3 AB	34 ± 2 C	32 ± 2 C	27 ± 3 D
Aerosil® 200	44 ± 3 A	37 ± 2 B	38 ± 3 B	31 ± 1 C	29 ± 3 CD
Aerosil® R972	44 ± 3 A	41 ± 4 AB	39 ± 2 B	39 ± 3 B	33 ± 1 C

Means followed by different letters differ from each other by Tukey Test ($p \leq 0.05$).

4. Discussion

The diffractograms of the resins with both clays (Figure 3) revealed the absence of exfoliation in groups containing 5%, 10% and 25% of these fillers. In the group with 2.5%, there was no peak d (001). This can be interpreted as reflecting an increase in the interlayer spacing to over 44 Å, being beyond the detection limit of the equipment. In this case, the system can be intercalated or exfoliated, requiring another technique to evaluate its configuration.

The dispersion of silicas can not be determined by XRD analysis because these fillers have spherical shape, because of these the silicas dispersion was determined by NMR analysis. Based on the XRD results, it can be determined that the increase in clay loading led to a decrease in the dispersibility of these fillers, this behavior has been reported in previous studies^[16,17]. This lower dispersion of clay is the cause of the increase in viscosity of these nanofillers, rather than their bare increase of loading. Another possibility relates to the increase of the number of particles in the system that generates a physical impediment to their dispersion, since there is limited space for a greater possibility of reunion and consequent agglomeration of these particles in more concentrated systems^[16,17].

The change observed in the groups with nanoclays is due to the type of distribution of these particles in the system. The increased temperature required for weight loss in the groups with lower clay loadings indicates that this system is exfoliated, corroborating the diffraction results. Similar studies have shown that this behavior results when these fillers are exfoliated. This fact can be attributed to the ability of layered structures to reduce the flow of gases within the material, and in this way, the heat flow^[18,19]. In the other groups, in turn, there was a reduction in the mass loss temperature, which probably occurred because of the degradation of organic modifier present in these minerals, something that occurs when these fillers are agglomerated in a polymer system^[20,21].

Thus, the LF-NMR analysis is in agreement with the results obtained by XRD, since the relaxation times also

show a possible exfoliated profile in mixtures containing 2.5% clay and the absence this at other loadings of these fillers. Similarly, the XRD showed that with loadings of 5% and 10%, secondary peaks appeared at angles smaller than the basal peaks. This finding, combined with the relaxation time reduction, confirms the presence of part of these fillers in the intercalated topology.

The reduction of relaxation times in the exfoliated configuration occurs because the clays used in the experiment were members of groups of montmorillonites characterized by high iron loadings. This compound causes a resonance effect, called a paramagnetic effect, which causes a change of the magnetic field reducing the relaxation periods of hydrogen nuclei of the polymer chains around the particles. Thus, exfoliated systems, because of their better dispersion, have more polymer chains under the influence of the paramagnetic effect. This causes a decrease in relaxation time, which is observed by LF-NMR^[22,23].

The explanations of this phenomenon are based on the presence of polymer chains around the clay layers, which brings the hydrogen nuclei of the paramagnetic metals that make up the clay layers nearer together. These metals act as relaxation agents, causing a decrease in the T₁H interval^[22,23]. In silica groups, the interaction between fillers and matrix reduces the mobility of the chains^[24]. Thus, a decrease in relaxation time can be expected. However, as previously noted, these fillers are agglomerated in the system. The cluster formation decreases the interaction between the nanoparticles and matrix, thus reducing the effect on relaxation time.

The results showed that addition of nanoparticles lead to reduction of DC for the evaluated systems. This behavior has been previously reported in other studies with different nanoparticles. The reduction of polymerization conversion in these cases stems from the increase in viscosity of the system^[25], which hinders the movement of its constituent during the polymerization, as well as, by the interaction of the nanoparticles with the light that can act as agents of the absorption and scattering of light, making the photoinitiation process less effective^[26].

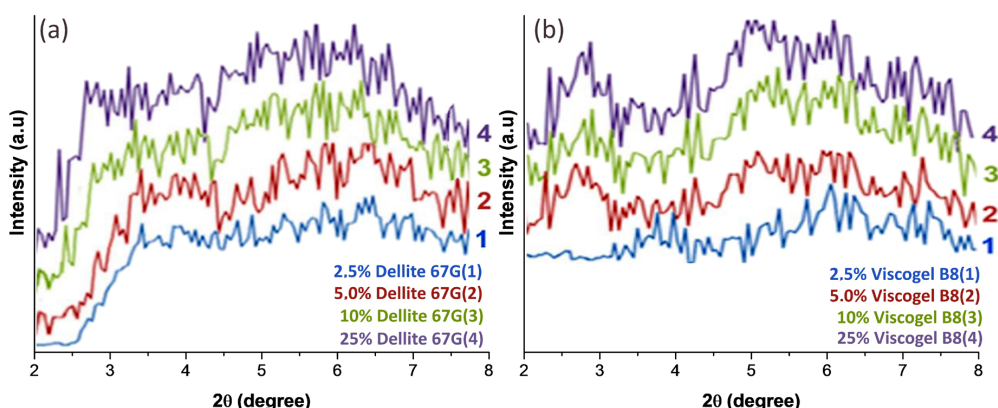


Figure 3. XRD patterns of (a) composites with nanoclay Dellite® 67G, (b) composites with nanoclay Viscogel® B8.

5. Conclusions

Based on the results, it can be concluded that:

- The groups with organoclay loading of 2.5% produced exfoliated material, a fact proven by the findings of the XRD and LF- NMR techniques;
- The clay fillers, when their loading was increased up to 5% and 10%, resulted into hybrid systems (partially exfoliated, partially agglomerated) and the groups with higher amounts of these fillers showed an agglomerated profile;
- All the groups containing silicas (hydrophobic and hydrophilic), were agglomerated and shows a poor dispersion when compared to the clays;
- The thermal resistance of the material was not affected by the fillers of Aerosil® 200 and Aerosil® R972, but improved when using 2.5% Dellite® 67G and 2.5% Viscogel® B8 and reduced with the addition of particles in the latter two groups of 5%, 10% and 25%;
- As the nanoparticles are added in the systems there is a gradual reduction of the composite DC indicating that the presence of these damages the polymerization process of the dental resins.

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