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Structural analysis on photopolymerized dental resins containing nanocomponents

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Abstract The incorporation of nanoscale layered silicates, as montmorillonite (MMT), into polymers has attracted great attention due to their ability to improve mechanical, thermal, and barrier properties of many polymers. Inserting these nanocomponents into dental resins could lead to materials with improved wearing resistance under masticatory attrition, among other advantages. Thus, the aim of this work was to investigate the process of incorporating layered silicates into dental resins by studying the influence of the concentration of these nanocomponents and the type of chemical species, used to modify the clays, in the morphology of the systems. Three types of clay were inserted in a BisGMA/TEGDMA photopolymerized resin system. The samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and small angle X-ray scattering (SAXS). FTIR and TGA results confirmed the presence of the modifier agents in MMT. SEM micrographs indicated a homogeneous distribution of the layered silicates throughout the dental resin after photopolymerization and a high degree of interfacial adhesion. SEM micrographs also showed that the mixing process used to add clay into dental monomers was not successful in breaking agglomerates and was also responsible for forming new agglomerates particularly in highly concentrated materials. XRD and SAXS patterns showed the development of a partially exfoliated/intercalated clay structure after photopolymerization of the dental resin. Exfoliation, together with intercalation, was even observed in materials having concentrations of MMT as high as 16 wt.%. Exfoliation in highly filled materials was attributed to the formation of a microstructure composed of large agglomerates, in which most of the MMT layers were concentrated and restricted to exfoliate, and few small particles disseminated throughout the polymer matrix that were able to exfoliate. SAXS results also suggested that the modification of MMT with species containing polar groups was more successful in producing exfoliated structures than MMT having highly hydrophobic incorporated species. The insertion of vinyl groups into MMT galleries led to the production of dental resins containing large and compact agglomerates with intercalated layers, as suggested by determining the fractal number of the materials. The possibility of producing photopolymerized dental resins containing exfoliated nanolayers can potentially be useful in controlling important properties of dental materials such as resistance to attrition, moisture absorption, polymerization shrinkage, coefficient of thermal expansion, among others.

Introduction

Dental composites have three main components: the resin matrix, the inorganic filler, consisting of particulates such as glass, and the coupling agent, that

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chemically bonds the reinforcing filler to the resin matrix. Despite vast improvements that have expanded indications for the use of dental composites, they still have shortcomings limiting their application. Inadequate resistance to wear under masticatory attrition is often cited as being a problem of dental composites that partially is responsible for reducing the life-span of the materials. Strength, stiffness, coefficient of thermal expansion, abrasion resistance, moisture absorption and shrinkage are dependent upon the filler and the coupling agent [1].

Clays have been recognized as potentially useful filler materials in polymer matrix composites because of their high aspect ratio and lamellar morphology [2]. These layered silicates, as montmorillonite (MMT), a clay mineral consisted of stacked silicate sheets separated by a regular spacing called gallery, have been used to produce structural engineering nanocomposites that combine both high strength and high toughness. Small quantities of this clay have shown dramatic improvements in mechanical, thermal, and barrier properties. The efficiency to improve these properties is determined by the degree of dispersion in the polymer matrix and the kind of bond between them. A particular feature of the MMT structure is that water and other polar molecules can enter between the units layers because of the relatively weak forces between them, causing the lattice to expand [3]. The nanocomposites formed can then be classified in intercalated and exfoliated. Intercalated state is termed when the polymer chains are inserted into the gallery space between the individual layers of the silicates, preserving the well-ordered multilayer structure of the silicate. Exfoliated state implies the structure where the interaction between the individual silicate layers no longer exists [4]. Because exfoliated nanocomposites have higher phase homogeneity and interfacial area than the intercalated counterpart, the exfoliated structure is usually more desirable in enhancing the mechanical properties of the materials. However, the majority of the polymer nanocomposites reported in the literature was found to have intercalated structures [3]. The hydrophilic nature of the surface of MMT restricts their homogeneous dispersion in the organic polymer phase. So, organic modifiers should be used to favor interactions between the silicate layers and the polymer [5, 6]. The organic treatments performed on the naturally hydrophilic minerals that render them organophilic, and hence enable compatibility with polymers, often introduce alkylammonium cations which also play a role in the resulting morphology. The size of the initial gallery separation of the silicates is affected by the size of the cations, used in ion-exchange processes, as well as upon the cation exchange capacity (CEC) of the silicate. Moreover, it has been proposed that the organic treatments may participate in the polymerization of the nanocomposite [7, 8]. Modeling studies of the melt intercalation of polymer into layered silicates have been reported and the phase-behavior of the polymer/clay nanocomposites has been treated theoretically [9].

The objective of this work was to study the process of incorporating layered silicates into photopolymerizable dental resins by analyzing the evolution of the morphology of the systems as a function of the composition and type of chemical species used to modify the clays. Structurally optimized dental nanocomposites containing layered silicates can then potentially show improved performance by allowing the control of properties related to attrition resistance, moisture absorption resistance, hardness, polymerizations shrinkage, etc.

Experimental procedure

Three commercially available types of montmorillonite (Cloisite® 20A, 30B and Na^+) purchased from Southern Clay Products were used in this study. They were received as fine particles with an average particle size of 6 μm. The MMT-20A and 30B are known to be ion-exchanged and, according to the producer, they are derived from MMT-Na^+. Vinylbenzyltrimethyl ammonium chloride 99% (abbreviation: VBTMAC) was purchased from Aldrich Chemical Company, and was used to modify the MMT-Na^+ surface to yield an organophilic clay containing vinyl groups (MMT-Vinyl). This modification was performed as follow [5]: a suspension of 25 g MMT-Na^+ in 1 L water was stirred overnight. To the suspension, an aqueous solution of 30 mmol VBTMAC, in 100 mL water was added drop wise. After stirring for 3 h at 0–5 °C, the precipitate was filtered, washed with water, methanol and ether, and dried in vacuum at room temperature.

The experimental composites were prepared by introducing the different types of clay into dental monomers. A mixture of 75 wt.% of a dimethacrylate base monomer (2,2-bis[2′-hydroxy-3′-methacryloxy-propoxy) phenylene] propane—Bis-GMA) and 25 wt.% of a dimethacrylate comonomer (tetraethylene glycol dimethacrylate—TEGDMA), both purchased from Polysciences, was handle stirred with each type of MMT for 20 min at room temperature. The different clays were added into the monomers in concentrations from 0.5% to 16% in weight. Canforquinone (1 wt.%) and 2-dimethylamine ethyl methacrylate (1 wt.%) were used as photo-initiators [10].

The polymerization was activated by irradiation. A dental light-curing unit (Degulux – Soft-Start®, Degussa/USA), equipped with one halogen lamp (75 W), was used to cure the materials. Samples with dimensions of 8 mm in diameter and 0.5 mm in thickness were prepared inside two plastic strips. The strips were used to contain the material and to prevent inhibition of surface polymerization due to the presence of oxygen. The samples were then photo-cured from the upper and lower surfaces, being submitted to 120 s each side, using an 800 mW/cm^2 light intensity. This intensity was always checked using a radiometer (Demetron 100, Demetron, Danbury, CT, USA). After being removed from the strips, the samples were stored in dark and dry conditions at 37 °C. The different types of modified MMT, used in this work, are listed in Table 1.

Original and modified clays were characterized by infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Infrared spectroscopic experiments were carried out on a Perkin-Elmer Spectrum 1000 Fourier transform infrared spectrometer (FTIR). Typically, 32 scans at a resolution of 4 cm^{-1} were recorded on each sample by using an ATR (Attenuated Total Reflection) apparatus. The inorganic content of the clays was determined using a TGA by measuring the weight of the samples left after heating up to 900 °C. The analyses were performed in a TGA 50H (Shimadzu) in dynamic N_2 atmosphere (100 mL min^{-1}) and 20 °C min^{-1} heating rate.

Scanning electron microcopy (SEM) micrographs of the dental resins containing layered silicates were obtained in a Jeol, JSM-6360 LV microscope. The images were taken from the fracture surface of the materials produced at cryogenic temperatures and covered with gold.

The periodic structure of silicate layers in the pure clays and in the nanocomposites was determined by X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) experiments. The XRD data were collected on a PW1710 Phillips diffractometer using CuKα (40 kV, 20 mA) radiation. The data was recorded in the 2θ range from 3° to 12.5°, in steps of 0.01° and counting time per step of 2 s. The measurements of Synchrotron SAXS were performed using the beam line of the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil). The photon beam used in the LNLS SAXS beamline comes from one of the 12 bending magnets of the electron storage ring. The white photon beam is extracted from the ring through a high-vacuum path. After passing through a thin beryllium window, the beam is monochromatized ($\lambda = 0.1608$ nm) and horizontally focused by a cylindrically bent and asymmetrically cut silicon single crystal. The focus is located at the detection plane. The reflection plane is (111), the asymmetry angle equal to 10° in condensing mode, the energy range is 6–12 keV (0.1–0.2 nm) and the energy resolution ($E/\Delta E$) is about 1,000 for typical detector-to-sample distance [11]. A set of slits defines the beam vertically. A position sensitive X-ray detector (PSD) and a multichannel analyzer were used to determine the SAXS intensity. The X-ray scattering intensity, $I(q)$, was experimentally determined as a function of the scattering vector "q" whose modulus is given by $q = (4\pi/\lambda)\sin(\theta)$, where λ is the X-ray wavelength and θ being half the scattering angle. Each SAXS pattern corresponds to a data collection time of 900 s. From the experimental scattering intensity produced by all the studied samples, the parasitic scattering intensity produced by the collimating slits was subtracted. All SAXS patterns were corrected for the non-constant sensitivity of the PSD, for the time varying intensity of the direct synchrotron beam and for differences in sample thickness. Because of the normalization procedure, the SAXS intensity was determined for all samples in the same arbitrary units so that they can be directly compared. The sample-detector distance of 551.6 mm was used during the measurements.

Table 1 Characteristics of the clays used in the study

Clays	MMT-Na$^+$	MMT-20A	MMT-30B	MMT-Vinyl
Organic modifier used	–	Dimethyl dehydrogenated tallow ammonium[a]	Methyl tallow bis-2-hydroxyethyl ammonium[a]	Ar-Vinylbenzyl trimethyl ammonium chloride 99%[b]
CEC meq/100 g	92.5	95	90	–
Number of tails	–	2	1	–
TGA (% inorg)[c]	87.35	58.75	68.21	79.36
XRD $d_{(001)}$ (nm)[d]	1.22	2.58/1.26	1.7	1.5
SAXS $d_{(001)}$ (nm)	1.2	2.5	1.8	1.5

[a] Introduced by the producer

[b] Introduced in our laboratory

[c] Percent of the original mass left after decomposition in temperatures up to 900 °C

[d] Interplanar distance (001) measured by XRD and SAXS

Results and discussion

Figure 1 shows the organic/inorganic content of the pure clays. It can be noted that the original clay (MMT-Na$^+$) had a lost of mass close to 10% in temperatures up to 120 °C due probably to evaporation of adsorbed water. Water lost in other clays was very small, indicating that the original clay should be more hydrophilic than the modified clays. The modified silicates showed variable loss of mass in the range between 300 and 400 °C due to the thermal degradation of the different organic species used to modify the original MMT. The amount of mass loss in this temperature stage can be related to the amount and size of organic modifiers incorporated within clay layers.

Figure 2 shows FTIR spectra of the clays. IR bands around 3,620, 3,430 and 1,640 cm^{-1} are related to the presence of hydroxyl groups in the clays. Bands related to organic groups, such as CH_3, CH_2, can be observed at 2,900, 2,800 and 1,470 cm^{-1} and prove the presence of the alkylammonium species incorporated into MMT-20A, MMT-30B and MMT-vinyl.

Figure 3 shows XRD patterns associated with the clays used in this work. The basal spacing for the original clay (MMT-Na$^+$) was determined from the d_{001} to be 1.2 nm. XRD pattern related to the organophilic MMT, called MMT-20A, showed that the d_{001} basal spacing shift to 2.58 nm as a consequence of the successful intercalation of the dimethyl dehydrogenated tallow ammonium ions. It was also possible to note the presence of a peak at $2\theta = 7.3°$ ($d = 1.26$ nm) that possibly is related to the gallery space of the original clay (MMT-Na$^+$). This result is an evidence that a small part of the clay was not intercalated during the ion-exchanged process performed by the producer. This interplanar distance changed to approximately 1.7 nm in MMT-30B as a result of the intercalation of a different type of alkylammonium ion. These results are consistent with the data provided by the supplier (Southern Clay). Figure 3 also shows that the ion-exchanged process performed to incorporate vinyl groups within the clay layers led to an increase in the d_{001} spacing from the original 1.2 nm (in MMT-Na$^+$) to 1.5 nm (in MMT-Vinyl).

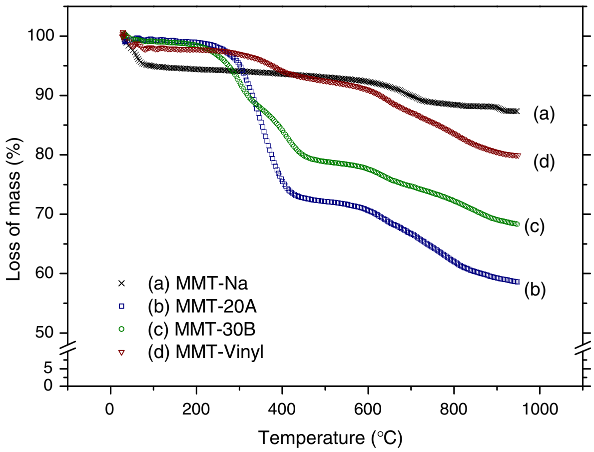


Fig. 1 Typical TGA scans for the original and organic modified clays

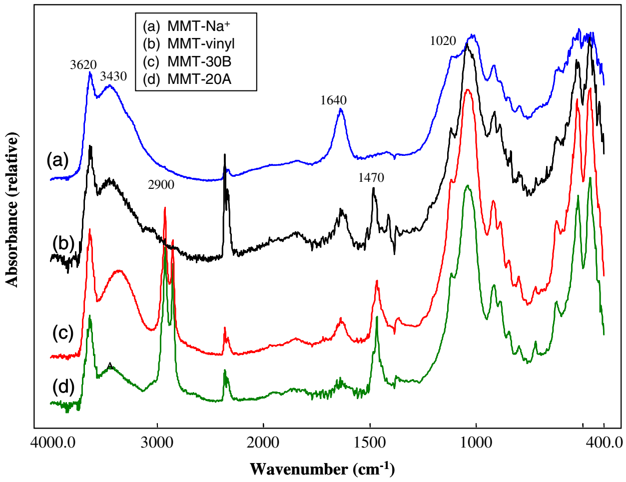


Fig. 2 FTIR spectra of the original and organic modified clays

SEM micrographs of composites containing lower (3%) and higher concentrations of the different types of clay (9%) are shown in Fig. 4. The micrographs indicate that a homogeneous distribution of the layered silicates throughout the BisGMA/TEGDMA matrix and the absence of voids were achieved. Large "tactoids" formed by agglomeration of the nanoparticles can be seen in all micrographs as a consequence of the poor capability of the handle stirring process to break agglomerates. Larger tactoids are more frequently found in composites containing the MMT modified with vinyl groups. It is possible that the chemical procedure, which included the incorporation of reactive species (such as compounds containing vinyl groups) onto the surface of clay sheets, could have promoted adhesion between particles, favoring the formation of larger agglomerates. A larger number of large tactoids can also be observed in materials having higher concentration of clay, as an indication that agglomeration could have occurred during the mixture of the components. One of these tactoids is shown again in the micrograph of Fig. 5. It is possible to observe that the surface of the agglomerate is very rough, being composed of many smaller flat units stacked. The micrograph in Fig. 5 is also useful in

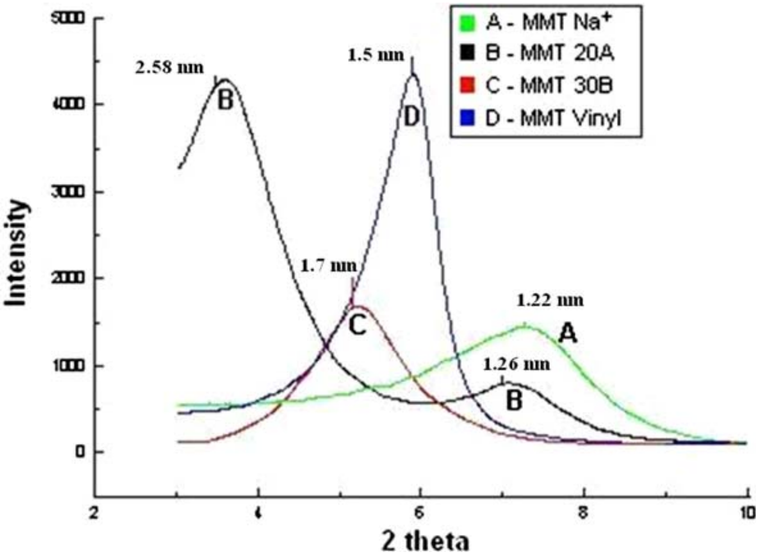


Fig. 3 XRD patterns associated with the clays used in this work

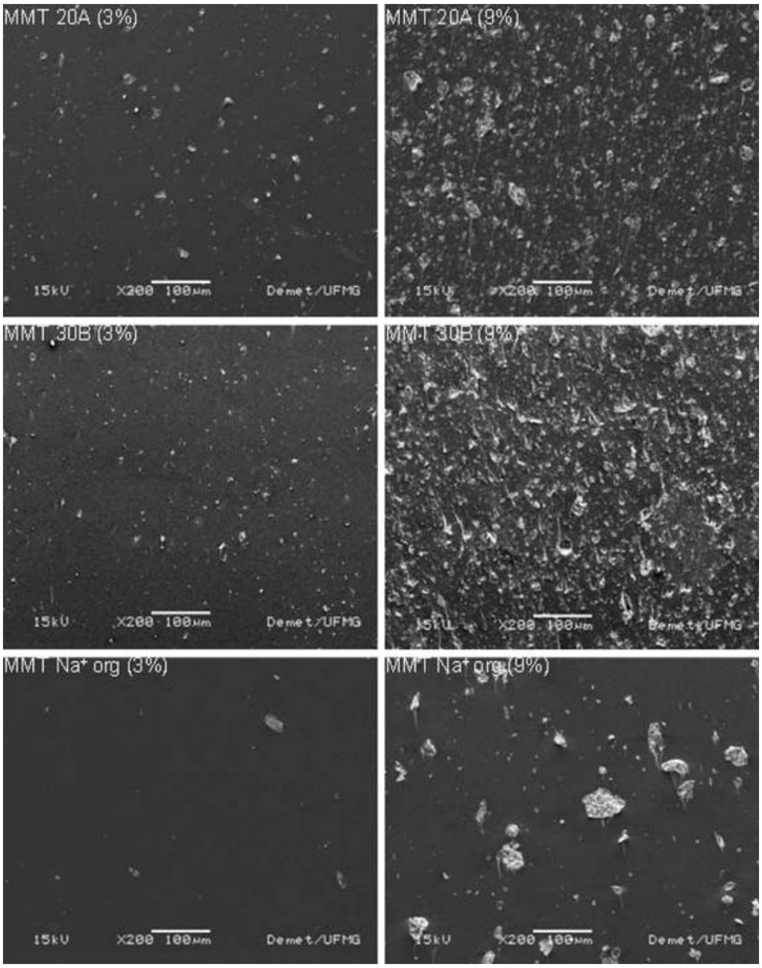


Fig. 4 SEM micrographs of a series of dental resins containing different types and concentrations of clay

evaluating qualitatively the degree of adhesion between particles and polymer. The fracture surface of the composite shows that particles remained incorporated within the polymer matrix after the fracture process (there was no particle pull-out). There are also no interfacial voids between particles and polymer, as an indication that no interfacial debonding occurred during crack propagation. The morphology of the

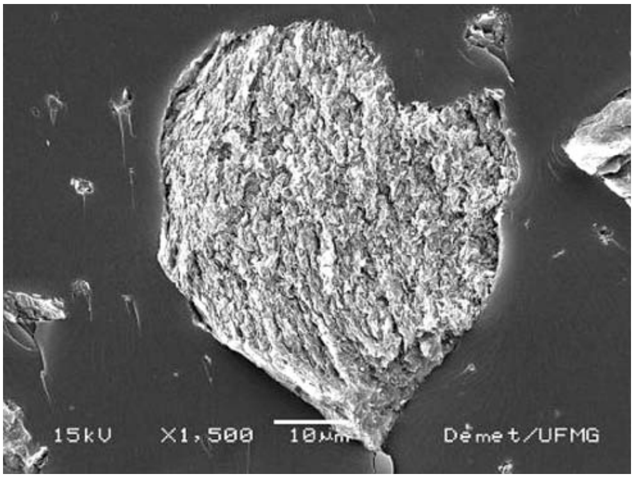


Fig. 5 SEM micrograph of a large agglomerate of the MMT-vinyl observed in dental resins containing 16 wt.% of the clay

fracture surface suggests that the preferred path of crack propagation occurred through the clay agglomerate and not through the interfacial region. This result can mean that the degree of interfacial adhesion is high enough to avoid debonding. This type of fracture surface morphology was observed in all samples containing the different clays used in this work, suggesting that all chemical species used to modify clay galleries were useful in allowing the formation of strong interfaces.

XRD patterns obtained after photopolymerization of the dental monomers containing the different types and concentrations of clays are revealed in Figs. 6–8. Figure 6 shows the XRD results of the system containing 9 and 16 wt.% of MMT-20A. The XRD patterns of these nanocomposites showed peaks at $2\theta = 5°$ (1.7 nm) and 7.3° (1.2 nm). The fact that the d_{001} peak (originally at $2\theta = 3.5°$ in MMT-20A) shifted to wider angles may be an indication that some of the clay layers became closer than in pure MMT-20A after being incorporated in the monomers and submitted to photopolymerization. This type of result will be further examined and clarified using SAXS.

Figure 7 shows the XRD patters associated with the nanocomposites produced using 9 and 16 wt.% of MMT-30B. These nanocomposites showed d_{001} values very close to the ones observed in pure MMT-30B (1.7 nm) that may indicate that no further intercalation was obtained when the MMT-30B clay was incorporated into Bis-GMA monomers. Figure 8 exhibits the XRD results for the materials obtained by incorporating the MMT-Vinyl into Bis-GMA based system. The measured d spacings for both nanocomposites containing 9 and 16 wt.% of MMT-Vinyl were close to 1.5 nm. This value of d spacing is also similar to the one observed in pure MMT-Vinyl, indicating that intercalation due to the presence of dental monomers was not further enhanced.

Fig. 6 XRD patterns of dental resins containing MMT-20A

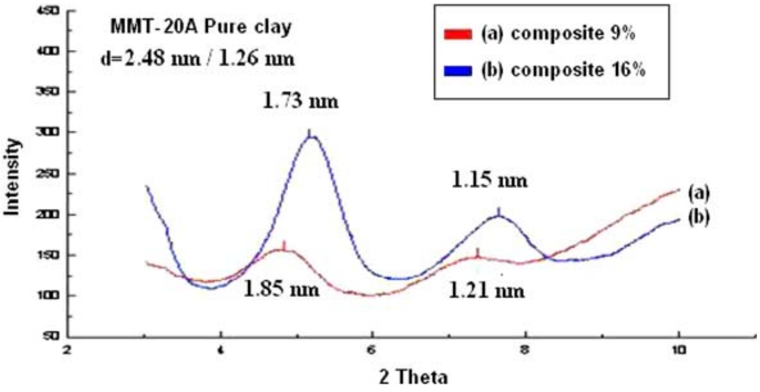
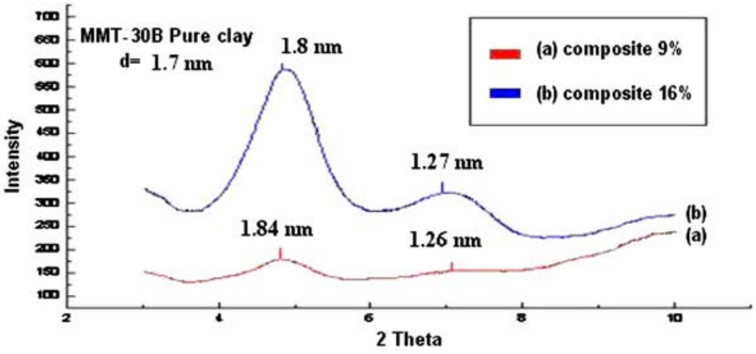


Fig. 7 XRD patterns of dental resins containing MMT-30B



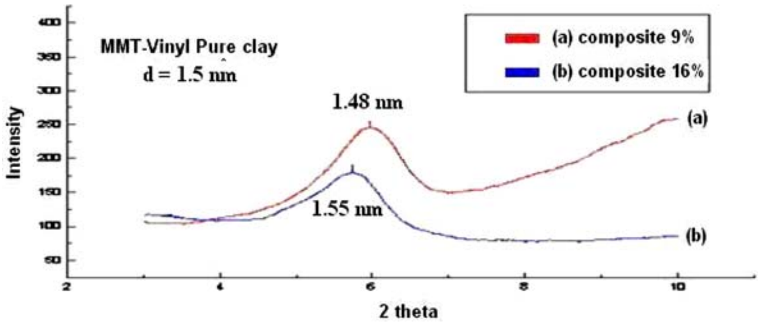


Fig. 8 XRD patterns of dental resins containing MMT-vinyl

SAXS is one of the most useful characterization techniques to study the morphology of polymer nanocomposites, block copolymers and segmented polymers [12, 13]. SAXS applied to nanocomposites formed by incorporating nano-clays into polymers has provided a series of information regarding the changes in phase morphology as a function of the composition and chemistry of the systems [3, 14].

A second phase of colloidal dimensions dispersed in a matrix of constant electronic density presents small angle X-ray scattering if there are differences in electronic densities between the phases. SAXS, as an analytical technique, involves measuring scattering intensity as a function of the angle measured with respect to the direction of the incident X-ray beam.

The characteristic scattering curves obtained from polymeric systems can be described within the formalism proposed by Beaucage [15, 16] that assumes the existence of a number of related structural levels by means of a unified equation, provided the range of experimentally observed q values is wide enough. The intensity would then obey the equation:

$$I(q) = G\exp\left(-\frac{q^2R_g^2}{3}\right) + B\left[\frac{\left\{\mathrm{erf}\left(qR_g/\sqrt{6}\right)\right\}^3}{q}\right]^P \qquad (1)$$

where the first term accounts for the Guinier region (values of $q \le 2p/R_g$), with two adjustable parameters: the Guinier prefactor G and the radius of gyration R_g. The second term describes the power law scattering behavior (for $q > 2p/R_g$). Porod's law predicts a value of $P = 4$ for the high q limit in the case of sharp interfaces. Values of P smaller than 4 are associated with diffuse interfaces. If $4 > P > 3$ the exponential law is characteristic of a fractally rough surface. The power-law exponent (P) can be calculated from the slope of the log–log intensity plots [17]. When P assumes a value $1 < P < 3$, the sample is a mass fractal. The various values in this range correspond to different types of mass aggregation and/or some polymeric structures with specific features [17].

In this work, the SAXS technique was used to provide information regarding the effect of both composition and the type of interfacial modifier (species intercalated within clay galleries) on the morphology of the silicate layers incorporated into photoactivated dental resins. In order to determine the exact SAXS peak positions, a mathematical procedure was used to filter the scattering information due to Bragg diffraction within a background due to Guinier type of scattering [4, 18]. This mathematical procedure involved fitting the experimental scattering data to a combination of an exponential decay function (Guinier scattering) and a Gaussian function (capable of identifying Bragg diffraction peaks). Figure 9 shows the usefulness of this mathematical procedure to enhance the resolution of scattering peaks. In this figure, the raw SAXS scattering data of a photopolymerized dental resin containing only 0.5% of MMT-30B is

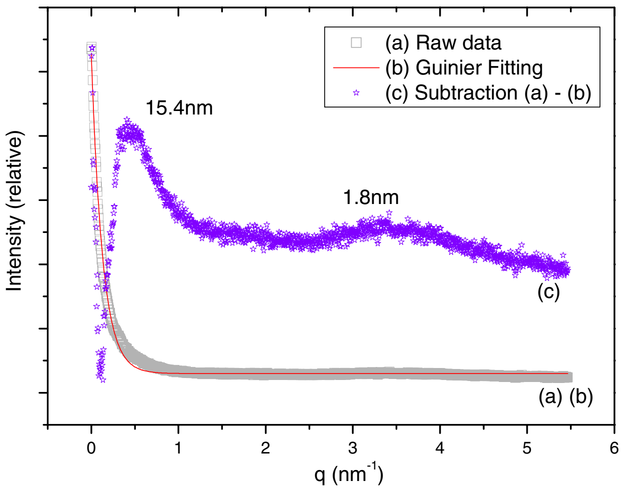


Fig. 9 Example of how SAXS data was explored in this work to enhance resolution of small scattering peaks: (**a**) raw SAXS data relative to a dental resin containing 0.5% of MMT-30B; (**b**) Guinier fitting of the raw data; (**c**) result of the subtraction between raw data and Guinier fitting

exhibited together with the fitting curve in which only the Guinier term was used during the calculations. The result of a subtraction between the original curve and the fitted curve is also shown in Fig. 9 to reveal clearly two major diffractions peaks having q values equal to 0.41 and 3.4 nm^{-1}. The position of the scattering peaks in SAXS intensity profiles can be related to the "d" spacing of the silicate structure by applying Bragg's equation [19–21]:

$$L = \frac{2\pi}{q_{\max}}, \tag{2}$$

where, $q_{\max}$ is the value of q at the maximum of the scattering peak. The SAXS values of the d spacing of the silicate layers in the dental resin containing 0.5% of MMT-30B are 1.9 and 15.4 nm.

Representative scattering data as a function of the scattering vector (q) for dental resins containing 0.5% and 16% of MMT-30B and also the pure clay are shown in Fig. 10. Diffraction peaks due to the interlayer spacing in clays can be identified in the curves while less intense peaks were revealed by the mathematical treatment described above. As it was noted before by X-ray diffraction, MMT-30B has a value of the basal spacing d_{001}, also determined by SAXS, close to 1.9 nm. Also shown in Fig. 9, the scattering data of dental resins containing small quantities of MMT-30B (0.5%) reveals two reflection peaks associated with interlayer spacing of 15.4 and 1.9 nm. This result may imply that some of the original MMT-30B clay particles have their interlayer distance expanded (from 1.9 to 15.4 nm) during monomer incorporation and subsequent photopolymerization to yield partially exfoliated structures. The periodicity seen in this type of exfoliated nanostructure is due to the steric interaction between silicate layers having anisotropic shape [18]. SAXS data associated with the dental resin containing 16% of MMT-30B show three major diffraction peaks that represent distances of 2.0, 4.4 and 21.3 nm. This result indicates that the contact of the clay particles with the dental monomers and also the photopolymerization process led to a mixture of partially intercalated (2.0 and 4.4 nm) and exfoliated clay particles (21.3 nm). Peaks corresponding to distances of 2.0 and 4.4 nm have positions ratios close to integral numbers, indicating that they may be originated from the same periodic structure of the silicate layers.

Figure 11 SAXS shows data for dental resins containing MMT-20A in several concentrations: 0.5, 9 and 16 wt.%. Scattering maxima were observed that define interlayer distances of 19, 42 and 21.3 nm for all nanocomposites with different formulations. As in the case of dental resins containing the MMT-30B, the photopolymerization of dental monomers in the presence of the MMT-20A clay led to the formation of a mixture of intercalated and exfoliated clay particles. It is interesting to note that the literature well-documents the fact that the presence of high contents of clay (usually higher than 5–10 wt.%) in polymers restrict the evolution of the morphology of the clay towards exfoliation due to spatial limitations that ends up keeping the clay layers close enough to allow the formation of strong interactions between adjacent silicate layers. In the SAXS results in Figs. 10 and 11, even dental resins filled with clays in concentrations as

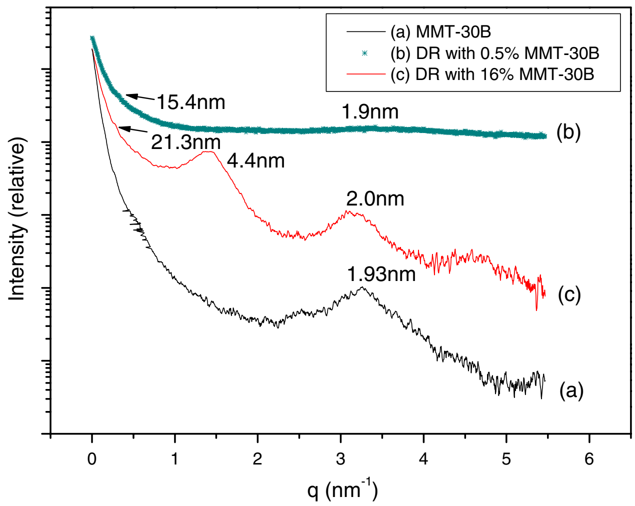


Fig. 10 SAXS data relative to MMT-30B (**a**) and dental resins (DR) having 0.5 wt.% (**b**) and 16 wt.% (**c**) of MMT-30B

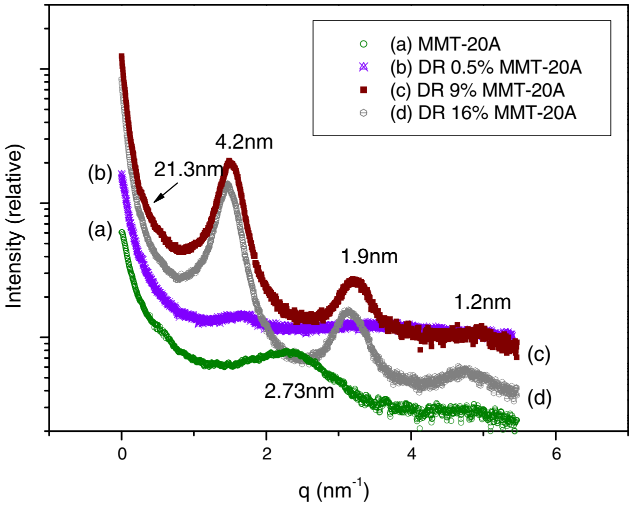


Fig. 11 SAXS data relative to MMT-20A (**a**) and dental resins (DR) having 0.5 wt.% (**b**), 9 wt.% (**c**) and 16 wt.% (**d**) of MMT-20A

high as 16 wt.% showed the presence of a partially exfoliated clay structure. This result can be explained by the fact that the process of mixing the clay with dental monomers did not involve the use of high shear forces. Thus, this type of mixing process led to not only to difficulties in dispersing initially present clay agglomerates but also allowed the formation of new larger agglomerates as it can be seen in the micrographs of Fig. 4. Clay layers within large agglomerates are spatially locked and then restricted to exfoliate. Only small particles not linked to large agglomerates were free enough to exfoliate. Therefore, in dental resins containing high concentrations of clay (such as 9 and 16 wt.%), only a small percent of this inorganic content not present in large agglomerates was actually able to exfoliate. In these cases, even large concentration of clay in polymers did not lead to volume saturation and the portion of the clay not present in large agglomerates could behave as in very dilute compositions.

SAXS data in Fig. 12 is associated with dental resins that were polymerized in contact with the MMT clay previously modified with vinyl groups. Results showed that, although a small diffraction peak that characterize distances between clay layers of 21.7 nm, was observed, no major shift in the original diffraction peak due to the clay was detected. In order to explain this result, it can be suggested that the reaction rate between vinyl groups incorporated within clay layers was different when compared to polymerization rate associated with the dental resin, resulting in either the formation of bridges between clay layers or the stabilization of the polymer network outside the clay galleries faster than inside them.

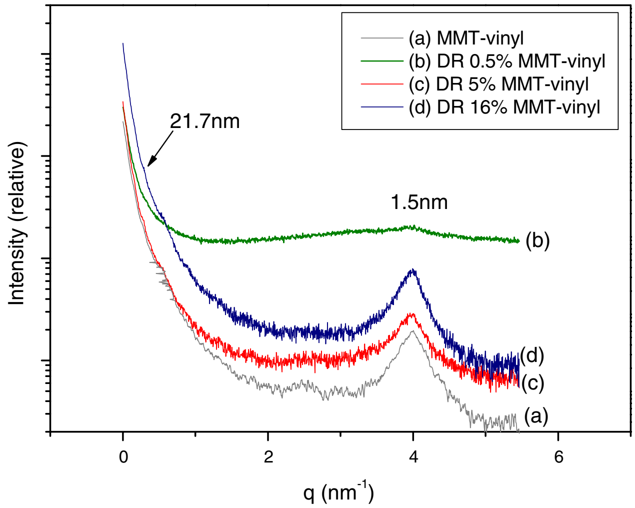


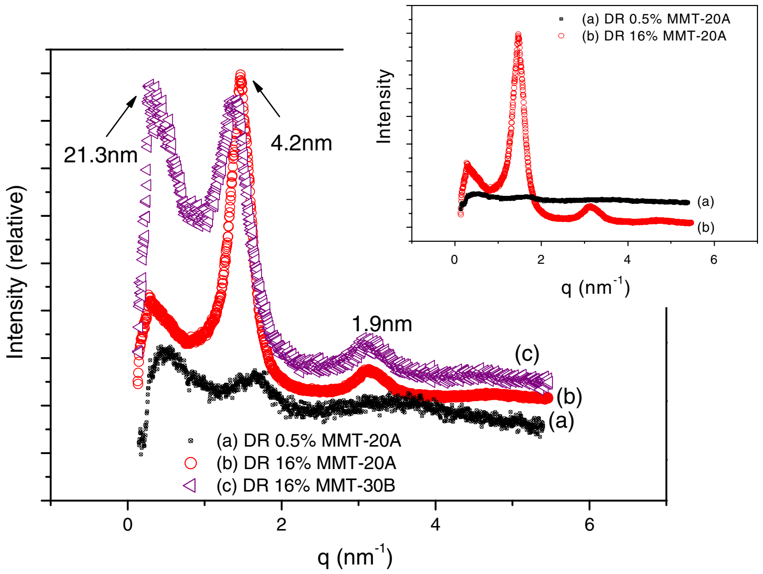
Fig. 12 SAXS data relative to MMT-vinyl (**a**) and dental resins (DR) having 0.5 wt.% (**b**), 5 wt.% (**c**) and 16 wt.% (**d**) of MMT-vinyl

Figure 13 compares the results of the subtraction between the original SAXS curves and the fitted curves for three different nanocomposites: dental resins containing 0.5% of MMT-20A, 16% of MMT-20A and 16% of MMT-30B. This comparison enables the verification of the effect of the concentration and type of clay in the proportion of intercalated and exfoliated clay within the dental resins. It is possible to observe that lower concentrations of the clay led to diffraction peaks due to exfoliated layers (21.3 nm) having a higher intensity than the peaks due to intercalated layers (4.2 nm). Agglomeration during mixing was again an important fact to be considered in this discussion. Agglomeration during mixing was progressively more observed in materials containing higher concentrations of clay (Fig. 4) due to the higher probability of interaction between particles during mixing of these formulations. Clay layers locked within agglomerates were less able to exfoliate than smaller particles dispersed through the polymer matrix and in between large agglomerates. Thus, materials having lower concentrations of clay had also lower concentrations of large agglomerates that would exhibit intercalated structures. They would then also have a more relevant portion of their composition distributed in non-agglomerate particles that could lead to exfoliation.

In Fig. 13, it is also noted that the MMT-30B led to diffraction peaks due to exfoliated structure more intense than materials with MMT-20A. This result may indicate that the interfacial modifier in MMT-30B, that has one alkyl chain and two hydroxy side groups, is more compatible with dental resins than the interfacial modifier used in the preparation of MMT-20A (that has two alkyl chains and a methyl side group). Dental monomers have ether linkages that are responsible for imposing some polarity to dental resins. Therefore, a not highly hydrophobic interfacial modifier in clays (such as in MMT-30B) may be more compatible with dental resins than a very hydrophobic interfacial agent (such as the one present in MMT-20A).

Figure 14 reveals the fractal number obtained by fitting the SAXS data to physical models as described in Eq. (1). The results clearly show that there is an increase in the fractal number for increasingly concentrated nanocomposites as an indication of the presence of more dense particles having better defined interfaces. The presence of large agglomerates containing intercalated polymer chains can also be related to the observed larger fractal numbers, since this fact was more frequently noted for more highly filled dental

Fig. 13 SAXS data processed by the mathematical treatment described in the text to enhance the resolution of small scattering peaks. (**a**) dental resin (DR) having 0.5 wt.% of MMT-20A; (**b**) dental resin having 16 wt.% of MMT-20A; (**c**) dental resin having 16 wt.% of MMT-30B. Inset: same curves (**a**) and (**b**) but plotted in a common scale to show the different levels of scattering produced by a highly filled dental resin (16 wt.%) and a dental resin with low concentration of clay (0.5%)



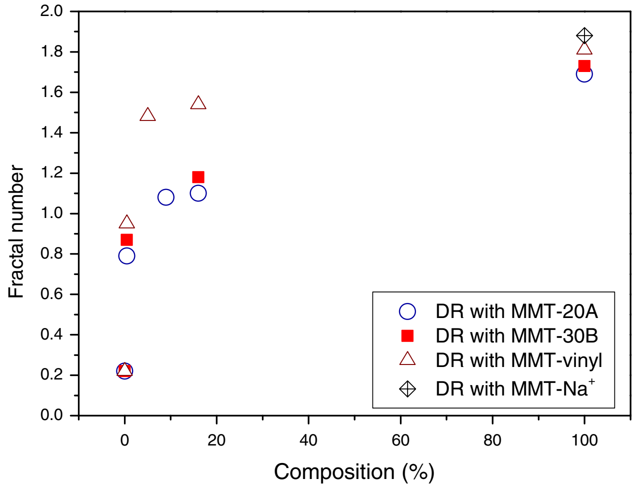


Fig. 14 Fractal number derived from SAXS data relative to dental resins containing different amounts of clays

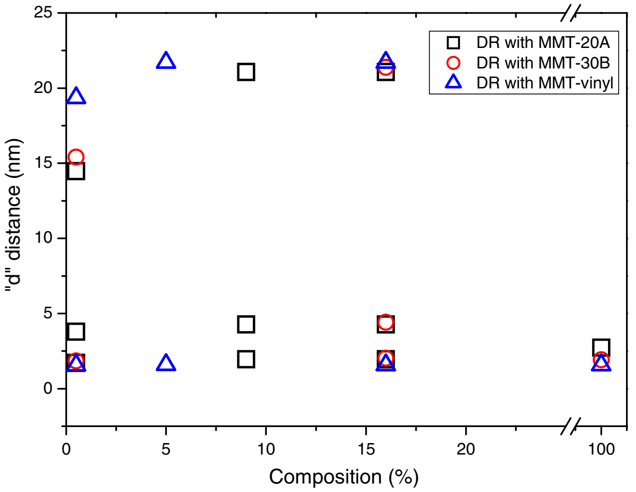


Fig. 15 Interlayer distance $d_{(001)}$ derived from SAXS data relative to dental resins containing different amounts of clays

resins. By comparing the fractal number of materials having the same composition, it is possible to observe that dental resins with MMT-vinyl have larger fractal numbers than other systems as another evidence of formation of more compact structures with less exfoliated particles. For the system containing MMT-vinyl, it is also possible to verify that the fractal number reached values close to the fractal number of the pure clay for compositions as low as 5 wt.%. This result again suggests that MMT-vinyl in larger concentrations in dental resins is behaving as conventional fillers that basically fill space with no major morphological changes.

Figure 15 summaries all the SAXS data to show again that the photopolymerization of dental resins led to generally the production of a mixture of exfoliated and intercalated structures. The proportion of each type of structure could be related to the type and concentration of clay as discussed above.

Conclusions

In this work, layered silicates derived from modified MMT were incorporated into conventional dental monomers that were subsequently photopolymerized to yield dental nanocomposites. Layered silicates having different types of chemical modifications were incorporated in different concentrations into dental polymers to result in the production of dental resins having a series of formulations. Thermogravimetric and infrared analyses were useful in demonstrating the presence of the organic chemical species incorporated into MMT. SEM micrographs revealed the formation of a microstructure in the dental resins composed of large agglomerates homogeneously distributed throughout the polymer matrix. XRD and SAXS data indicated the presence of a mixture of partially exfoliated and intercalated clay layers within the dental resins. SAXS results showed that exfoliation was even observed in highly filled materials, as a consequence of the presence of large agglomerates that accumulate a large portion of the incorporated clay. In this case, the fraction of the clay present as small particles was spatially free to exfoliate. Vinyl groups incorporated into MMT galleries led to the production of materials containing almost only intercalated clay layers as possibly a result of different reaction rates involving vinyl groups inside and outside the clay galleries that can result in the formation of strong covalent bridges between layers. Chemical modification of the clays with species containing polar groups was more successful in producing materials with a larger concentration of exfoliated layers than when MMT with highly hydrophobic species were used. This result can be explained by the fact that dental resin has polar groups (such as ether linkages) within its structure that can interact with polar unit grafted on the surface of clay.

The ability to incorporate layered silicates into photopolymerizable dental resins in at least partially exfoliated structures can be useful in manipulating a series of characteristics important to improve the performance and life-span of dental composites, such as resistance to attrition, resistance to moisture absorption, control of polymerization shrinkage, among others.

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