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Evaluation of flexural modulus, flexural strength and degree of conversion in BISGMA/TEGDMA resin filled with montmorillonite nanoparticles

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Abstract

This study had as its main objective to evaluate the flexural properties (strength and modulus) and degree of conversion of a dimethacrylate resin containing different amounts of nanoparticulated clay Montomorillonite (MMT) as filler. A series of composites containing similar amounts (in volume) of barium glass particles was also tested as control data. Eight formulations with polymeric matrix-based BisGMA/TEGDMA (Bisphenol A Bis(2-hydroxy-3 methacryloxypropyl)Ether/Triethyleneglycol Dimethacrylate), four added with MMT and four added with barium glass in the volume concentration of 20, 30, 40 and 50 vol% were studied. The degree of conversion was determined using near-IR spectroscopy. Elastic modulus and flexural strength were determined by the three-point bending test. The dispersion of MMT nanoparticles was determined by means of X-ray diffraction and transmission electron microscopy analysis. The fillers montomorillonite and barium glass interacted with polymer matrix-based BisGMA/TEGDMA in a distinct manner. Although the addition of montomorillonite nanoparticles resulted in similar degree of conversion and higher elastic modulus values at all concentrations tested, only at the 20 vol% the flexural strength was statistically higher, compared to the control groups filled with barium glass. This could be related to the need of concentration optimization of montomorillonite for each type of polymer matrix in order to adjust or improve mechanical properties. The addition of low concentrations (<l 20% vol) of montomorillonite nanoparticles in dental composites resins – such as additive or hybrid filler – should be studied, aiming to the reduction of polymerization shrinkage, better mechanical properties and improvement of a new technology for future applications.

Keywords

Nanoclay, nanocomposites, mechanical properties, strength, X-ray diffraction

Introduction

Dental composites are versatile materials which use is growing continuously since their introduction on dental market about 50 years ago.[1] In 1963, Bowen developed a monomer named glycidyl methacrylate of Bisphenol-A (BisGMA). The BisGMA monomer has a long aliphatic chain connected to a pair of aromatic rings. It reduces polymerization shrinkage and enhances the rigidity and stability of the resulting mass, and since then, it is the most used polymer for dental restoration. To reduce the BisGMA viscosity ($\eta = 1369\,\text{Pa·s}$), dimethacrylate was added as a co-monomer. The

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decrease of viscosity allows the interaction of the filler particles (initiators, inhibitors and filler particles), but also increases the polymerization shrinkage of the composite.[2,3] Due to the aesthetics benefits and direct technique, resin composite is the main material used for dental restorations.[4,5]

However, dimethacrylate-based composites present some disadvantages such as high water sorption and solubility which decrease restorations' longevity,[6] and polymerization shrinkage, frequently associated with an increase in the elastic modulus, known to generate stresses on tooth/restoration interface, post-operative sensitivity, and secondary caries.[7] In order to minimize these problems, filler particles (such as quartz, silica, and barium glass) are added in the resin matrix to improve mechanical properties and reduce polymerization shrinkage, constituting 75–85 wt% of the material.[8]

Recently, the development of filler particles with nanometric dimensions allowed for further improvements in restorative dental composites. The addition of nanoparticles on dental composites was shown to improve wear resistance, gloss retention,[9] elastic modulus,[10] flexural strength, diametral tensile strength[11,12], and to reduce polymerization shrinkage.[13]

Montmorillonite (MMT) nanoparticles, known in the automobile, packing, and aerospace industries for providing excellent mechanical and thermal properties,[14–16] can be seen as an alternative to the filler particles commonly used as reinforcing phase in dental composites. MMT nanoparticles have a crystalline lamellar structure consisting of layers, being a central octahedral layer of alumina intercalated by two layers of tetrahedral silica. These layered silicates consisted of stacked silicate sheets separated by a regular spacing called gallery (or basal spacing "d") have nanometric thickness (about 1 nm) and width ranging between 100 and 1000 nm.[17–20]

Although there are few studies in the literature using nanoclay in dental composites, the results showed that the addition of MMT in these materials reduced polymerization shrinkage[20,21] and residual stress,[18,22,23] as well as improved wear resistance and resistance to solvent absorption.[20] According to some authors, the ability of MMT to absorb organic molecules increases the inter-lamellar spacing and provides additional volume within the material during polymerization. The authors' hypothesis was that expansive nature of the clay could reduce the magnitude of polymerization shrinkage and residual stress of the composites.[18,23]

This absorption ability represents a great advantage in dentistry, and the MMT association with dimethacrylate resin matrices used in dental composite formulations is still poorly explored. According to a previous study,[24] a decrease of polymerization shrinkage was observed in experimental composites with high concentration of MMT (50–70%wt), compared to groups filled with the same concentration of conventional filler (silanized silica). In addition, there is no report in the literature about mechanical properties (flexural strength/ elastic modulus) with the same polymeric matrix and MMT nanoparticles used in the present study, even at low filler concentration.

Therefore, the aim of this study was to evaluate the degree of conversion and flexural properties (strength and modulus) of a dimethacrylate resin containing different amounts of MMT nanoparticles. As control, a series of composites containing similar amounts (by volume) of silanized barium glass particles (BG) was also tested. The null hypothesis was that the evaluated properties were not affected by the amount of MMT nanoparticles and were similar for both types of filler.

Materials and methods

Two series of experimental composites were formulated, both with the same resin matrix (1 BisGMA : 1 TEGDMA, in mols), and 20%, 30%, 40% or 50% (volume) of filler. The photo initiator and tertiary amine corresponded to 2% (volume) of all formulations tested. The first series used MMT nanoparticles, while in the second group the reinforcing phase was constituted by silanized barium glass particles (2 μm). Table 1 shows the materials used in composite formulation.

Filler particles were incorporated in the polymeric matrix with the assistance of a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA). The entire manipulation process of experimental composites was performed under yellow light.

MMT Cloisite® 30B nanoparticles used in this study, according to the manufacturer, were organophilizated by surface functionalization. Other information about MMT nanoparticles can be observed in Table 2. Concerning the Barium Glass, according to the manufacturer was silanized (5.66%) and interfacial adhesion between the filler particles and polymeric matrix was promoted by the silane groups containing in the surface.

Degree of conversion

Degree of conversion (DC) ($n = 5$) was determined using near-IR spectroscopy (Vertex 70, Bruker Optik, Germany). Disc-shaped specimens were made using a silicon mold (h = 0.8 mm, Ø = 7.0 mm) between two glass slides. FTIR spectra were recorded before and 10 min after photo activation, using two scans per spectrum at a resolution of 6 cm^{-1}. The composite was photo-cured for 40 s, using a LED curing light (Kondorteck's Aigh-7A LED, at 470 nm wavelength, commonly used to the dental composite cure). Degree

Table 1. Materials used in experimental composites formulations.

Material	Function	Manufactured
Bis-GMA *(Bisphenol A Bis(2-hydroxy-3 methacryloxypropyl)Ether)*	Monomer Base	Esstech, Essington, Pennsylvania, USA
TEGDMA *(Triethyleneglycol Dimethacrylate)*	Co-monomer	Esstech, Essington, Pennsylvania, USA
DMAEMA: *(2-(Dimethylamino)ethyl methacrylate)*, 98%	Co-initiator	Sigma-Aldrich Chemie, GmBH, Steinheim, Germany
Camphorquinone, 97%	Photo Initiator	Sigma-Aldrich Chemie, GmBH, Steinheim, Germany
Cloisite® 30B: MMT Natural	Filler	Southern Clay Products, Texas, USA
Barium Glass Silanized	Filler	FGM, Joinville, SC, Brasil

Table 2. MMT nanoparticles description (according to the manufacturer).

Nanoparticle	Organic modifier	Interplanar distance (d_{001})	CEC meq/100 g	Particle size (%)
MMT Cloisite® 30B	Methyl tallow bis-2-hydroxyethyl quaternary ammonium (MT2EtOH)	18.5 nm	90	$\leq$2.0 μm (10%) $\leq$6.0 μm (50%) $\leq$13.0 μm (90%)

of conversion was determined by assessing the change in area of the absorbance peak at 6165 cm $^{-1}$, corresponding to the first overtone of the methacrylate vinyl stretch in relation to the uncured material.[25,26]

Flexural modulus and flexural strength

Specimens $10 \times 2 \times 1$ mm ($n = 10$) were built using a split steel mould. Ten minutes after photo activation using the same parameters described for degree of conversion, the specimen was removed from the mould and subjected to three-point bending in a universal testing machine (Instron 5565 Canton, MA, USA), with 8 mm distance between the supports and at a cross-head speed of 0.5 mm/min. Based on the linear portion of the load × displacement curve, flexural modulus was calculated according to equation (1).[25,27–29]

$$E = \frac{L \times D^3}{4 \times w \times h^3 \times d} x\ 10^{-3} \tag{1}$$

where E is the flexural modulus (GPa), L is the load recorded (N), D is the span between the supports, w is the width of the specimen, h is the height of the specimen and d is the deflection corresponding to L (all in mm).

Flexural strength was calculated according to equation (2)[25,27–29]

$$\sigma = \frac{3 \times F \times L}{2 \times b \times h^2} \tag{2}$$

where σ is the flexural strength (MPa), F is the maximum load recorded before fracture (N), L is the span between the supports (mm), b is the width of the specimen (mm) and h is the height of the specimen (mm).

X-ray diffraction (XRD)

The interaction between the polymer matrix and the clay nanoparticles was evaluated by XRD in all the groups containing MMT. The interlamellar spacing "d_{001}" peak is characteristic for the nanoclay. MMT Cloisite® 30B has "d_{001}" = 1.82 nm. Changes in the interlamellar spaces refer to the intercalation effect associated to interaction clay with polymer, in the case of the composites.

XRD diffratograms were obtained using a PAN analytical brand, model X'Pert PRO with X'Celerator detector, Rigaku D with Cu Kα radiation ($\lambda = 1.54186$ A, 45 kV, 40A) at room temperature, the diffraction were scanned from 1.17° to 40° in 2θ range with 0.03° step at step/time 100s.

The interlamellar spacing was calculated according to Bragg's equation.[30]

$$\boldsymbol{n\lambda = 2d_{hkl}\sin\theta} \tag{3}$$

In which n is an integer, λ is the incident wavelength, d is the spacing between the planes of same {hkl} (Miller index) in the crystal lattice, and θ is the angle between the incident ray and the crystal plane.

Transmission electron microscopy

The specimens for transmission electron microscopy (TEM) analysis were ultramicrotomed into 60-nm-thick slices with a diamond knife in a Leica Ultracut UCT Ultramicrotome and the ultrathin slices were cut and collected on 200-mesh copper TEM grids. Transmission Electron Microscopy was determined using a JEOL Electron Microscope – JEM 1010.

Scanning electron microscope (EDS)

The scanning electron microscope analysis (SEM) allowed the observation of the morphology of the experimental composites containing MMT inorganic load. It is a form of analysis commonly used for studying surface structures in materials, due to the construction of three-dimensional images with high resolution and good depth of field, which implies there is no loss of sharpness. Analyses were performed on microscope Quanta 600 FEG, FEI brand, equipped with X-ray spectrometer by energy dispersive (EDS) Quantax 400 (SDD technology – Silicon Drift Detector) and Sprit software, Bruker brand. The stipulated work routine included the collection of secondary images for morphological characterization of the particles. The samples were adhered to double-sided tape of carbon, coated with platinum and fixed in a support for SEM.

Statistical analysis

Data for degree of conversion and elastic modulus were analyzed using two-way ANOVA/Tukey's test. Data for flexural strength were analyzed using Kruskal–Wallis/Tukey's test. For all tests, the global significance level was 5%.

Results

Means for degree of conversion (DC) and flexural properties are shown in Table 3 and standard deviations in Figure 1. Representative FTIR spectra of DC can be observed in Figure 2 and displacement × force representative curve of flexural properties can be seen in Figure 3. For DC, the interaction between factors was statistically significant ($p = 0.034$). Composites containing barium glass showed no statistically significant among filler contents, while for the MMT composites, the addition of 50 vol% of the nanoparticles resulted in a lower degree of conversion compared to the other materials with MTT. For a similar filler level, DC was statistically similar for both types of filler, except for the concentration of 40 vol% that resulted in higher DC for the MMT composite.

Regarding flexural properties, the interaction between filler type and content was significant for both strength and modulus ($p = 0.018$). Flexural modulus increased with filler content for the composites containing MMT nanoparticles, but the only significant difference was observed between 20 vol% and 40 vol%. Among composites containing BG, an increase in modulus was observed between 30 and 50 vol%. Regarding filler types, the groups with MMT nanoparticles showed higher flexural modulus, except at 50 vol% where both fillers displayed similar modulus.

Among the groups filled with MMT, the flexural strength results were similar at 20% and 30% (v/v). However, lower value was achieved at 50 vol%. At 40 vol%, the material shared similar characteristics between all groups containing MMT. With regard to the addition of BG, a relevant difference was observed for the group containing 20 vol%. By comparing the two types of filler, the groups with MMT nanoparticle showed a value statistically similar in relation to the groups added with BG at a concentration of 20 vol%, while lower values were observed at concentrations of 40 and 50 vol% and similar values were observed for all groups tested containing 30 vol% of filler. At 30 vol% BG, the material presented similar values to all groups tested.

Diffratograms of the MMT powder, as well as the MMT nanoparticles added to the resin matrix are shown in Figure 4. The diffraction peak interlamellar

Table 3. Means (with standard deviation in parentheses) for degree of conversion (%), elastic modulus (GPa) and flexural strength (MPa).

Filler content (vol%)	Degree of conversion (%)		Flexural modulus (GPa)		Flexural strength (MPa)	
	MMT	Barium glass	MMT	Barium glass	MMT	Barium glass
20	**72.6** (2.0)^{Aa}	**65.0** (6.7)^{Aa}	**1.40** (0.48)^{Ba}	**0.35** (0.26)^{Bb}	**55.6** (8.6)^{Aa}	**32.0** (13.1)^{Ba}
30	**71.1** (5.5)^{Aa}	**65.6** (6.0)^{Aa}	**1.91** (0.51)^{ABba}	**0.49** (0.18)^{Bb}	**33.7** (12.1)^{ABa}	**55.9** (18.1)^{ABa}
40	**71.6** (3.5)^{Aa}	**63.1**(6.3)^{Ab}	**2.50** (0.65)^{Aa}	**1.02** (0.5)^{ABb}	**30.5** (5.3)^{ABb}	**66.7** (25.5)^{Aa}
50	**61.5** (6.8)^{Ba}	**61.4** (4.9)^{Aa}	**2.00** (0.74)^{Aa}	**1.47** (0.55)^{Aa}	**23.5** (6.4)^{Bb}	**65.2** (18.0)^{Aa}

Note: For each variable, in the same line, means followed by the same lowercase letter are statistically similar. In the same column, means followed by the same uppercase letter are statistically similar.

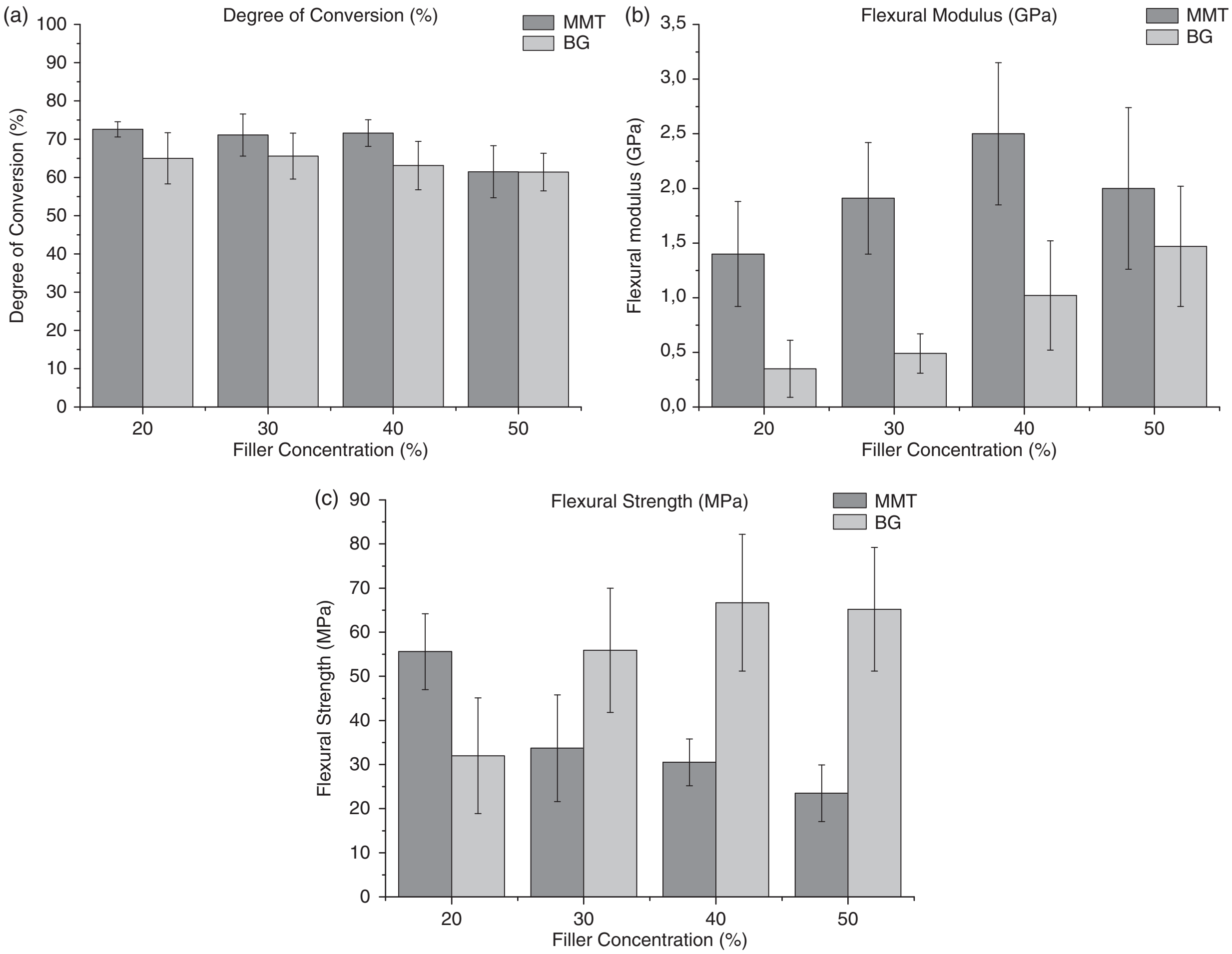

Figure 1. Means for (a) degree of conversion (%); (b) flexural modulus (GPa); (c) flexural strength (MPa).

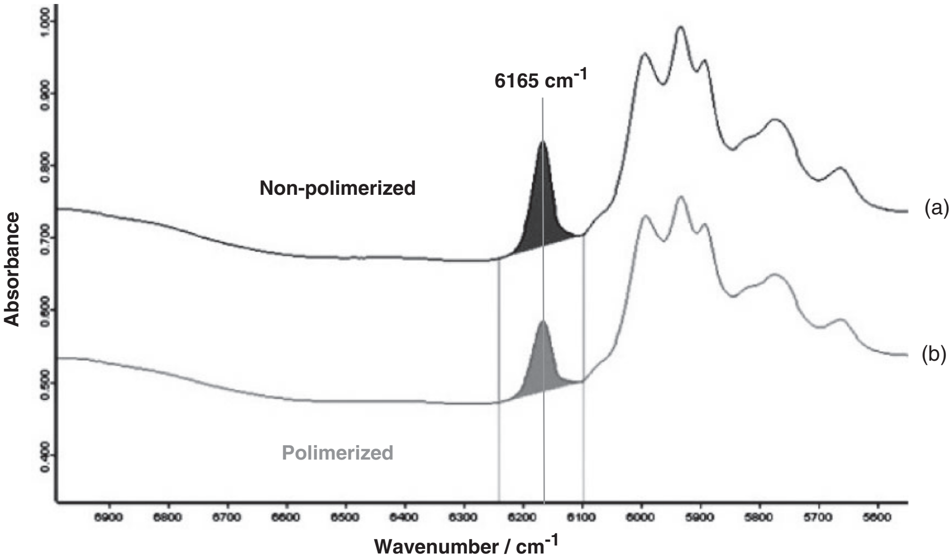

Figure 2. Representative FTIR spectra. (a) Non-polymerized and (b) polymerized peak at 6165 cm^{-1}.

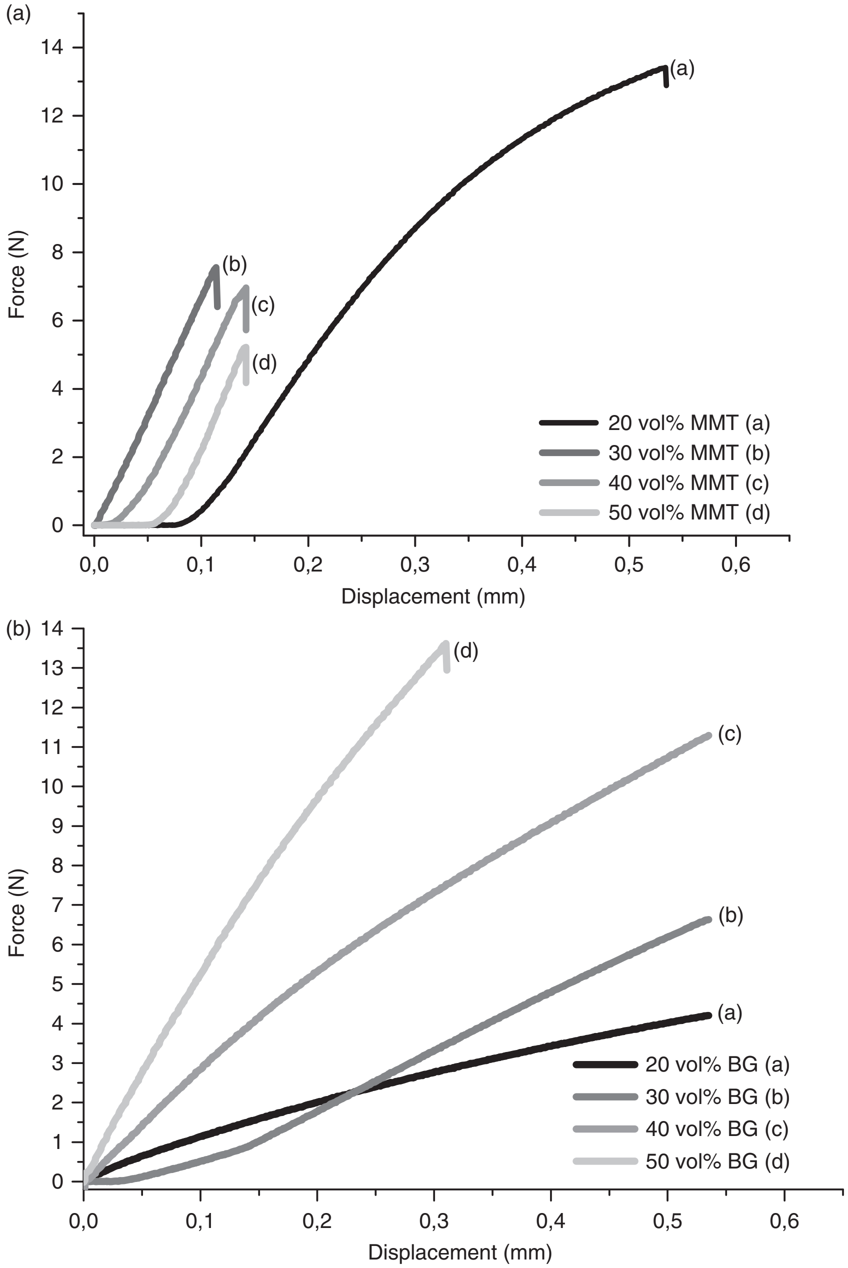

Figure 3. Displacement × force representative curves of flexural properties. (a) Curves of experimental composites filled with MMT and (b) filled with BG.

spacing of the 'pure' MMT was calculated as $d_{001} = 1.82$ nm. The 'd' values for the MMT filled on the polymeric matrix were: $d = 3.77$ nm for the composites containing 20 vol% MMT; $d = 3.68$ nm for the composites containing 30 vol% MMT; $d = 3.58$ nm for the composites containing 40 vol% MMT and $d = 3.57$ nm for the composites containing 50 vol% MMT. The displacement of 2θ peak (related to the interlamellar spacing 'd_{001}') for smaller angles was observed. That displacement of the inicial 'd_{001}' peak for smaller angles for both groups characterized the entry of the polymer into the clay layers in intercalation form, predominantly.

The intercalation phenomena observed by XRD analyses was confirmed in the Transmission Electron Microscopy images (Figure 5) where the polymeric matrix enters between the silicate layers (indicated by arrows).

In addition, there seems to be another amount of clay that remains in agglomerated form, identified (XDR) by the peak in the same region of pure clay $d = 1.82$ nm, credited as excess clay, i.e. a certain

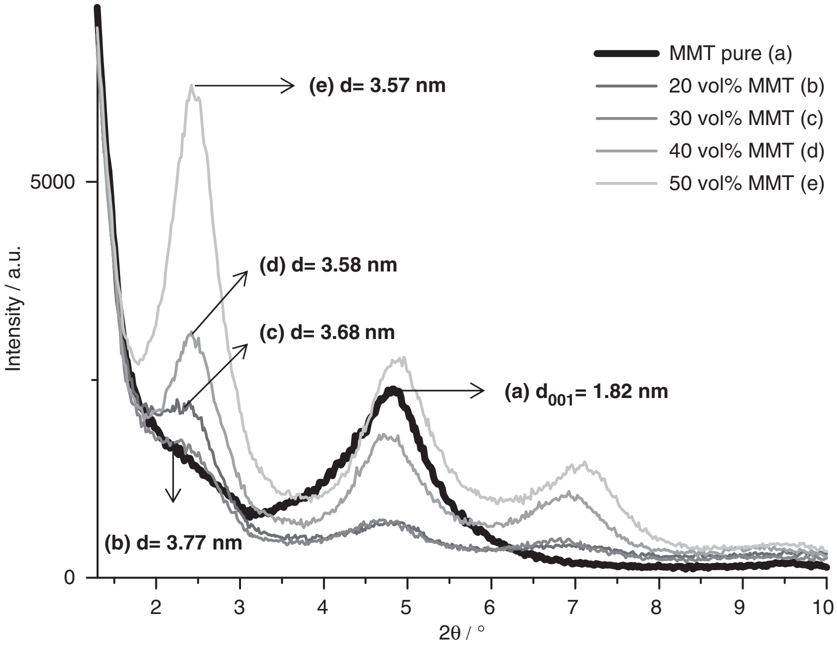

Figure 4. XRD patterns of MMT 30B pure and experimental composites groups filled with 20, 30, 40 and 50 vol% of MMT.

amount of clay had no intercalation with the polymeric matrix, leaving its lamellar structure almost unchanged. Small clusters of MMT nanoparticles were observed in SEM images (Figure 6), demonstrating that MMT has a tendency for clustering. Thus, the TEM and SEM images corroborate with the data obtained by XRD.

In spite of the limitation involved in the mixing of the experimental composites, the dispersion of the nanoparticles and absence of voids were noticeable for all the analyzed groups.

Discussion

According to the results obtained (Table 3), similar degree of conversion was observed for all concentrations in composites with BG. The absence of statistical difference among different filler content has been reported in a previous study.[31] At concentrations of 20, 30 and 40% in volume, the composites added with MMT were statistically similar. The only exception corresponded to the group containing 50 vol% MMT that had a lower degree of conversion when compared to the other groups added with the same filler type. This may be related to the size, filler concentration and refractive index that interfere in the dispersion of light and thus in the depth of cure and degree of conversion.[32]

For a given filler level, the degree of conversion of the groups using BG and MMT (Table 3) was statistically similar, except at a concentration of 40 vol%. These results suggest that the degree of conversion of experimental composites was not affected by the type of interaction between the MMT nanoparticle and a polymer matrix. In other words, there was no interference in the scission of carbon double bonds responsible for the monomer conversion. Other studies reported no alterations in the monomer conversion in matrix-based BisGMA/TEGDMA filled with MMT nanoparticle.[20,21,24]

Composites containing both types of filler showed an increase in the flexural modulus as the filler concentration increased (Table 3), in accordance with previous studies.[27] The increase in flexural modulus values due to an increase in filler generally follows the rule of mixture.[33] Composites filled with BG showed flexural modulus values similar to those reported in other studies.[31] Meanwhile, the experimental composites filled with MMT had higher flexural modulus than the BG groups, except for the materials with 50 vol%, which were statistically similar.

This higher flexural modulus found with the MTT composites values may be related to high stiffness and high modulus of the lamellar silicate particles.[34] In addition, the nanoparticles have greater contact surface with the organic phase, which can result in increase in the mechanical properties.[35,36] According to the literatures,[37–40] elastic modulus describes the relative stiffness or rigidity of a material and it is measured by the maximum deformation at the elastic region considering the stress–strain diagram. The flexural strength represents the maximum strength of a material during the flexural test prior fracture. The magnitude of the

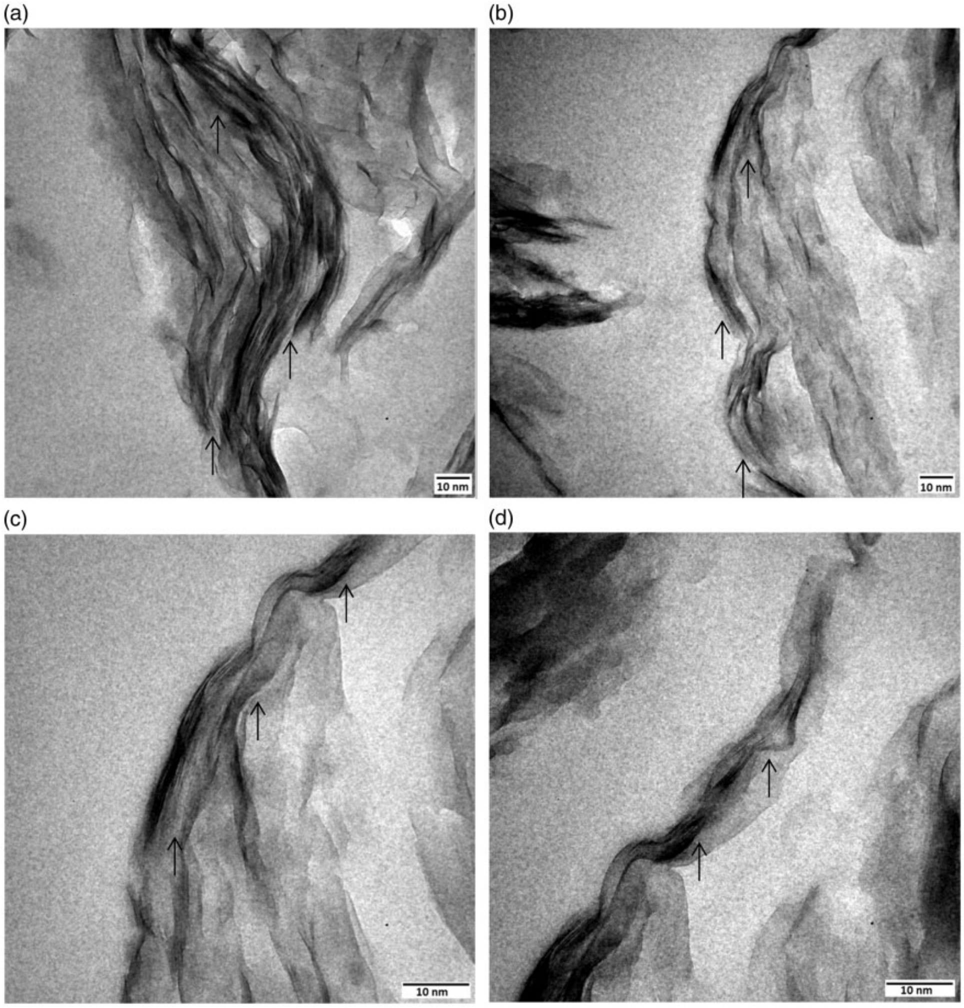

Figure 5. TEM images of experimental composites added with 30% of MMT nanoparticle. (a) and (b) with 75.000× magnification. (c) and (d) with 150.000× magnification.

elastic modulus affects the stress generated during composite resin cure. Flexural modulus and adhesivity properties play important roles inhibiting microleakage and secondary decay. The flexural modulus for occluso-proximal cavities must be high to resist cusp fractures and deformations.

The chemical affinity between an oxygenated polymer matrix based on BisGMA/TEGDMA and the polar functionalized MMT nanoparticle, might have been decisive for the flexural values obtained. According to Discacciati et al.,[23] the organic treatments realized on the hydrophilic minerals (organophilization process) makes MMT compatible with polymers. This modification also leads to expand the basal spacing between the silicate layers due to the presence of alkyl chain intercalated in the interlayer.

For polymer containing polar functional groups, an alkyl ammonium surfactant is adequate to promote the nanocomposite formation.[41] According to a previous study, [24] vinyl groups (from polar polymeric matrix) incorporated in the MMT lamellae lead to intercalated nanocomposite formation, resulting in the formation of strong covalent bonds between layers. The MMT nanoparticle when modified with polar groups (surfactants) favours the formation of exfoliated layers, when compared to the MMT modified with hydrophobic groups. This behaviour can be explained by the polar groups' presence in the polymeric matrix of dental composites that may interact with polar groups of the MMT surface. The lamellae adjacent to polymerization prevent folding due to electrostatic attractive forces between the quaternary ammonium ion and its negative counterpart, whereas Van der Walls forces between the organics fragments of quaternary ammonium ions work against exfoliation.[24,42]

Furthermore, XRD/TEM analyses showed predominantly intercalation effect of MMT nanoparticle

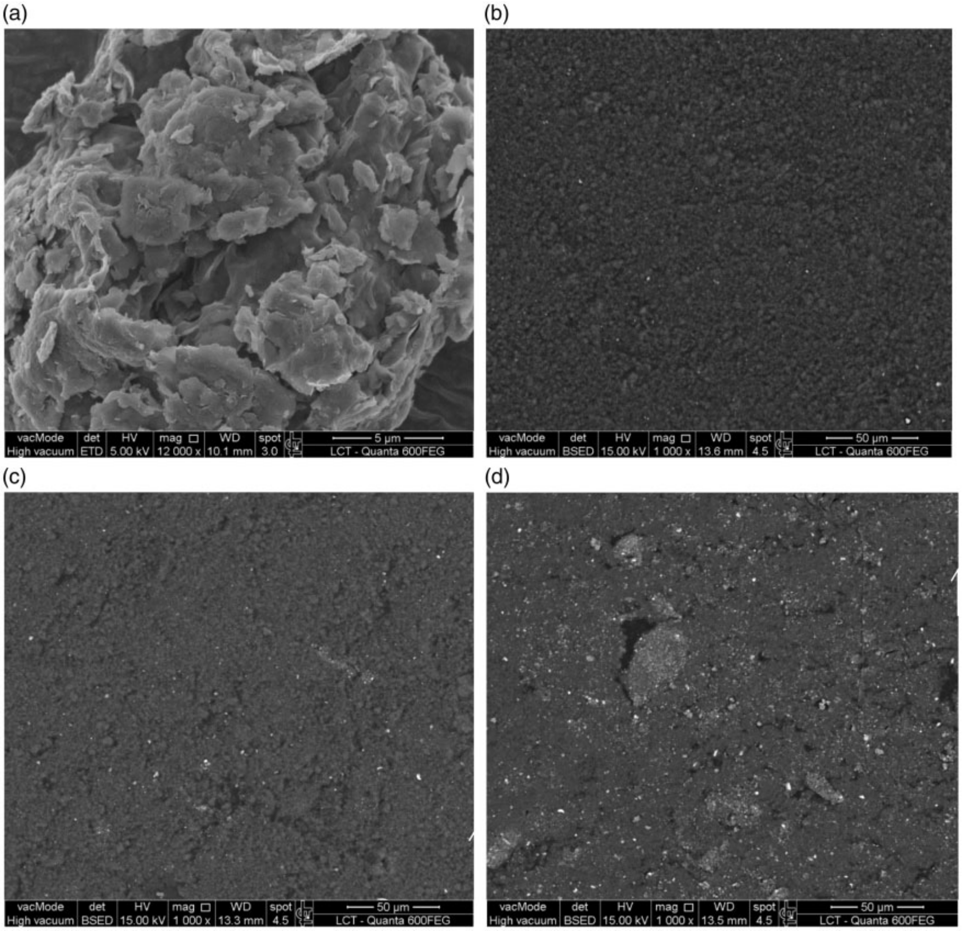

Figure 6. SEM/EDS images concerning to the MMT 30B pure (a) and experimental composites filled with 30 vol% (b), 40 vol% (c) and 50 vol% MMT (d). White dots indicate the presence of tactoids.

in relation to polymeric matrix for all groups, as previously observed in other studies.[20,24,42] An intercalated structure is defined when a single or more extended polymer chains are intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternated polymeric and inorganic layers.[17] This type of interaction filler–matrix being stronger and more stable than the interaction that occurs with BG, can result in an increase in properties as evidenced in the results of the flexural modulus analysis. Up to 40 vol% concentration, the flexural modulus values were statistically higher than the composites added with BG.

The composite containing 50 vol% MMT showed the lowest elastic modulus values compared to the others MTT-filled materials and this behaviour may be related to its lower degree of conversion. The reduction in the degree of conversion also led to a reduction in mechanical strength.[43] The agglomeration of MMT nanoparticles in the polymer matrix, observed in SEM images, may have contributed to this result. The white spots highlighted in the SEM images are associated with silicon molecule, one of the main MMT nanoparticle constituents. Thus, the larger the amount of white spots (silicon) suggests the presence of MMT agglomerates.[21] In addition, through the images scale it can be observed that the average size of tactoids was about 2 µm, characteristic of clusters. These results corroborated with previous studies in which the authors observed the formation of a great number of tactoids in experimental dental composites containing above 16 wt% MMT.[20] After it reached the optimum maximum level, the nanoparticles loading led to an induced aggregation state of nanoclay particles and reduced nanoparticles dispersion in the polymeric matrix.[19,44]

Regarding mechanical tests, flexural strength analysis was elected due to the strong correlation with fracture toughness methodology, which is used to simulate and predict the dental composite clinical behaviour on the oral environment.[29,45] Through the flexural strength analyses, the composites filled with MMT nanoparticle and BG showed different behaviours (Table 3). It was observed that for the MMT groups, strength decreased as filler concentration increased, while for the BG groups the opposite behaviour was found, in accordance with previous studies.[31] At high MMT levels, the formation of agglomerates (clusters) decreases the reinforcement efficiency. According to Hussain et al.,[34] the particle agglomeration (MMT) is the primary reason for the decrease in the strength of the material, even if the agglomerate is strong enough to significantly increase the elastic modulus.[34]

In addition, the agglomerates can act as stress raisers, reducing the failure strength of the material.[46] Agglomeration also reduces the intercalation effect, which further compromises the mechanical properties.[47] In a previous study, a large number of agglomerates were observed in materials containing above 60 wt% of MMT[24] which justify the maximum percentage used in this study.

Flexural strength decreased because functionalization of MTT was not sufficient to form adherent strong interface between filler and polymeric matrix (at high clay concentrations). Thereby, they act as defects within the composites that may act as crack initiation sites. The increase in MMT's content also increases the risk of crack initiation. This could be related to the need of concentration optimization of MMT for each type of polymer matrix in order to adjust or improve the mechanical properties.[21,44,46,48]

Conclusion

Based on the results obtained in this study, it can be concluded that despite fillers, MMT and BG interact with polymer matrix-based BisGMA/TEGDMA in a distinct manner, and both cases showed a degree of conversion statistically similar. The experimental composites filled with MMT presented flexural modulus higher at all concentrations tested and it could be related to the high modulus of the MMT nanoparticles and the intercalation effect of nanoparticles in relation to polymeric matrix, as observed in XRD/TEM analyses; regarding flexural strength, 20 vol% MMT was the only group that showed the higher value if compared to composites added with BG. The decrease in the resistance value with increasing concentration of filler can be attributed to the agglomerates formation (clusters), which decreases the reinforcement efficiency and this could be related to the need of concentration optimization of MMT for each type of polymer matrix, in order to adjust or improve the mechanical properties. The addition of low concentrations (<20% vol) of MMT nanoparticles in dental composites resins – such as additive, hybrid filler or partial replacement – should be studied, aiming to the reduction of polymerization shrinkage, better mechanical properties and improvement of a new technology for future applications.

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Declaration of Conflicting Interests

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