

Evaluation of polymerization shrinkage in dental restorative experimental composites based: BisGMA/TEGDMA, filled with MMT

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ABSTRACT: This work concerns to the investigation of the polymerization shrinkage and mechanical properties in dental restoratives experimental composites filled with nano clay Montmorillonite (MMT) Cloisite[®] 10A nanoparticles, in glycidyl methacrylate resin, using experimental composites filled with silanized Aerosil OX-50 Silica as a control group. Six formulations with BisGMA/TEGDMA based polymeric matrix (three added with MMT and three added with silanized silica as filler) containing 50, 60, and 70 wt % were investigated. Characterization of the experimental composites was established with the following analyses: Scanning Electron Microscope, (SEM); Thermo-Mechanical Analysis, (TMA) for Shrinkage Polymerization; Differential Scanning Calorimetry Analysis (DSC); Knoop Micro Hardness analysis; X-ray Diffraction (XRD); Degree of Conversion (DC); Elastic Modulus and Flexural Strength; Transmission Electron Microscopy (TEM). Statistical Analyses were realized using two-way ANOVA (type and amount of filler) and Tukey's test. TMA results showed that composites filled with MMT nanoparticle present statistically lower polymerization shrinkage values and statistically high degree of conversion in all formulations tested, when compared to composites filled with silanized silica. XRD and TEM analyses showed evidences of the intercalation phenomenon in the MMT nanoparticles in relation to BisGMA/TEGDMA polymeric matrix. However, for Flexural Strength, groups filled with MMT nanoparticle showed statistically lower values in all concentration tested. At high filler concentration it was observed the appearance of tactoids and functionalization of MMT nanoparticle did not promote a strong interface adhesion between polymeric matrix and filler. In order to adjust the mechanical properties, it would be convenient to promote the concentration optimization of MMT nanoparticles. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43543.

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INTRODUCTION

Aesthetics plays an important role in dental restoration in present days. Since composite resin begun to replace metal amalgams as the main material used for direct dental restorations, its main advantages over previous materials rely on the easier conservative cavity preparation as well as its ability to mimic teeth colors, providing superior aesthetic results.¹ However, this material undergoes significant polymerization shrinkage during curing, i.e., a change in free volume due to the reduction of the distance between macromolecules during polymerization. Some shrinkage drawbacks are residual stresses that lead to microcracks formation on the tooth-restoration interface, resin detachment from the remaining tooth, postoperative sensitivity and cusp deflection.^{2,3}

Considerable advances have been made recently in the dental composite field, attempting to produce more wear-resistant

materials with higher elastic modulus via structural changes, mainly by multifunctional methacrylate monomers and higher inorganic filler additions. Up to 85 wt % of filler particles (such as quartz, silica or barium glass) can be added in the resin matrix to improve its mechanical properties and reduce polymerization shrinkage to values as low as 1.5%.^{4,5}

Mineral clays, such as Montmorillonite (MMT) have already been studied as polymer fillers, with previous results in the plastic industry due to optical, thermal and mechanical properties improvement.⁶ Clays comprise a lamellar structure (composed of stacking layers, or lamellae) with thickness of ~1 nm, but length and width ranging from 100 nm to 1 μ m.⁷

Clay lamellar structure is responsible for their capacity to absorb different kinds of molecules. This absorption process occurs due to the higher surface area, compared to usual fillers

Table I. Formulations of Experimental Composites Groups

	Mass (mg)					
	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
BisGMA	248	198	148	248	198	148
TEGDMA	248	198	148	248	198	148
Canphoroquinone	2	2	2	2	2	2
DMAEMA	2	2	2	2	2	2
Cloisite [®] 10A	500	600	700	-	-	-
Aerosil OX-50 [®]	-	-	-	500	600	700
Total mass	1000	1000	1000	1000	1000	1000

and its volumetric expansion apart when the molecules, such as solvents, monomers or polymers penetrate in-between the lamellae. Whether sufficient amount of polymeric chains displace the lamellae, they can keep the stacking layout known as intercalated structure, or disperse throughout the matrix, process known as exfoliation.⁸ In both intercalation and exfoliation, clay layers act as anchors, restraining the polymeric chains mobility and directly affecting the free volume and composite modulus.

Several authors studied the effects of layered silicates and clays nanofillers on reducing or controlling polymerization shrinkage and residual stresses for different matrixes over the last decade.^{1–13} Mostly taking advantage of the afore mentioned clay properties in reducing polymerization shrinkage and enhancing composite mechanical properties.

The present work aims to evaluate the effect of Cloisite[®] 10A MMT clay nanoparticles on polymerization shrinkage and mechanical properties in BisGMA/TEGDMA experimental composites containing 50, 60, and 70 wt % of filler and to compare it with composites containing the same relative amount of conventional silanized silica filler.

MATERIALS

The following materials were used in the polymeric matrix preparation: BisGMA: (Bisphenol A bis(2-hydroxy-3-methacryloxypropyl)ether) manufactured by Esstech (Essington, USA); TEGDMA: (Triethyleneglycol Dimethacrylate) produced by Esstech (Essington, USA); Camphorquinone: (camphorquinone, 97%) provided by Sigma-Aldrich (Germany); DMAEMA: (2-(Dimethylamino)ethyl methacrylate), 98% purchased from Sigma-Aldrich (Germany).

As inorganic filler, the following materials were used: natural Cloisite[®] 10A MMT, manufactured by Southern Clay Products, USA; Silanized Aerosil[®] OX-50 Silica, provided by FGM, BRA.

Cloisite[®] 10A MMT

Mineral clay Cloisite[®] 10A MMT used in this study, according to the manufacturer, was previously made organophilic through surface modification by dimetil benzyl hydrogenated tallow (2MBHT) quaternary ammonium chlorine, with a concentration of 125 meq per 100 g⁻¹ of clay. Tallow refers to a mixture of alkyl compounds with approximately 65% in weight of C₁₈,

30% of C₁₆ and 5% of C₁₄. Cloisite[®] 10A MMT has $d_{001} = 1.92$ nm as the main X-ray diffraction initial peak, which also indicates its interlamellar spacing.¹⁴

Silanized Aerosil[®] OX-50 Silica

The silanized silica compound used in this study is constituted by particles with a radius of 0.04 μm . Its surface area, according to the manufacturer, is 26.2 m²/g.

METHODS

Samples

Composites were prepared by manual mixing for the homogeneous incorporation of inorganic filler into polymeric matrix according to reported procedures.^{13–18} Six groups of experimental composites were prepared from a BisGMA/TEGDMA base (1:1) with camphorquinone (1 wt %) and DMAEMA (1 wt %). After manipulation of the polymer matrix, the inorganic filler (MMT 10A or silanized silica) was added in small amounts until complete incorporation according to formulations (shown in Table I) for each group. For adequate mixture, every experimental composite was grinded for 5 min until not identify, visually, any filler agglomeration in the polymeric matrix.

Scanning Electron Microscope (SEM)

The scanning electron microscope analysis (SEM) allowed morphology observation of the experimental composites containing mineral clay inorganic filler. 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. Analyses were performed on microscope Quanta 600 FEG, FEI brand. The samples were previously adhered to double-sided tape of carbon, coated with platinum and fixed in a support for SEM.

Thermo-Mechanical Analysis (TMA)

The TMA/SDTA840 quartz sensor measured the real time polymerization shrinkage and dimensional changes of samples during the cure process with a precision of 0.1 μm .³ This method measures the total polymerization shrinkage along a single axis.¹⁹ Polymerization was monitored for a total time of 5 min, in which the light activation started after equilibrium of 30 s. During the photo polymerization (3 minutes), the TMA recorded the main volumetric changes of the samples. Ten samples were tested for each group ($n = 10$). The test was

established in isotherm program, at 25 °C, operating simultaneously to the photo polymerization LED Curing Light, Kondor-teck, model Aigh-7A, under photo excitation at 468 nm wavelength, commonly used to the dental composite cure.

Differential Scanning Calorimetry (DSC)

The monitoring of cure and post cure of composites were performed through calorimetry. The thermal enthalpy event attributed to the post-cure of the composites was investigated, after the polymerization, by DSC 822 Mettler –Toledo operating with 20 mg samples in aluminum pan, heating program from 25 to 300 °C, in dynamic atmosphere of N₂ at 50 mL min⁻¹ and heating rate of 10 °C min⁻¹. All DSC experiments were done in duplicates. The absence of exothermic events in DSC indicates complete cure of the experimental composites.

Knoop Micro Hardness

Micro hardness analysis were performed on a Shimadzu, model HMV 200. The applied load was set 25 g for 10 s and the area analyzed was limited to the length of the longest diagonal of the Knoop indenter marks left on the tested samples.²⁰

X-ray Diffraction (XRD)

The purpose of this analysis was to determine the interaction level between polymeric matrix and MMT nanoparticles and interlamellar distance (basal spacing) of the Montmorillonite added to the BisGMA/TEGDMA polymeric matrix, in the experimental composites containing MMT Cloisite[®] 10A nanoparticle.

Initially a XRD patterns was obtained for pure MMT Cloisite[®] 10A nanoparticles, followed by those of the experimental polymer/MMT composites. As such, a comparison was made possible between the interlamellar distance for pure MMT, “*d*₀₀₁”, and that for each other case, “*d*”. It was also possible to evaluate the type of interaction between the MMT and the polymer. Experimental composites filled with silanized Aerosil OX-50[®] silica (control groups) were not subjected to XRD analysis because silica is a noncrystalline material.

XRD patterns were obtained using a PAN Analytical, model X'Pert PRO with X'Celerator detector, Rigaku D with Cu K α radiation ($\lambda = 1.54186$ Å, 45 kV, 40A) at room temperature. The diffraction covers the angles from 1.17° to 40° in 2θ range with 0.03° step at step/time 100 s. The interlayer spacing was calculated according to Bragg's equation.²¹

$$n\lambda = 2d_{hkl}\sin\theta \quad (1)$$

where *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.

Degree of Conversion (DC)

Degree of conversion (DC) (*n* = 5) of the experimental composites was determined using near-IR spectroscopy (Vertex 70, Bruker Optik, Germany). Disc-shaped specimens were made using a silicon mold (*h* = 0.8 mm, \varnothing = 7.0 mm) between two glass slides. FTIR spectra were recorded before and 10 minutes 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 (Radii Cal, at 440–480 nm wavelengths,

commonly used to the dental composite cure). Degree 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.^{22,23}

Elastic Modulus and Flexural Strength

Specimens 10 × 2 × 1 mm (*n* = 10) were built using a split steel mold. Ten minutes after photo activation using the same parameters described for degree of conversion, the specimen was removed from the mold and subjected to three-point bending in a universal testing machine (Instron 5565 Canton, MA), 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 x displacement curve, flexural modulus was calculated according to the eq. (1).²²

$$E = \frac{L \times D^3}{4 \times w \times h^3 \times d} \times 10^{-3} \quad (1)$$

where *E* is the elastic 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 the eq. (2)

$$\sigma = \frac{3 \times F \times L}{2 \times b \times h^2} \quad (2)$$

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), *h* is the height of the specimen (mm).

Transmission Electron Microscopy (TEM)

The specimens for 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.

Statistical Analyses

Data were analyzed using two-way ANOVA (type and amount of filler) and Tukey's test. For both tests the global significance level adopted was 5%.

RESULTS

Scanning Electron Microscope (SEM)

A stacking characteristic can be seen as well, with a greater magnification, as the layers seems to be placed on top of each other. This behavior demonstrates the lamellar structure of the composite, in which clay layers are separated by interlamellar spacing, “*d*” with polymer in-between. Figures 1–3 show SEM images for the pure MMT and for those from groups 1, 2, and 3 containing mineral clay MMT nanoparticle with 1.000, 4.000, and 12.000× magnification, respectively.

Thermo-Mechanical Analysis (TMA)

Polymerization shrinkage results, obtained from TMA analyses for the experimental composites containing MMT and silanized silica, can be found in Table II.

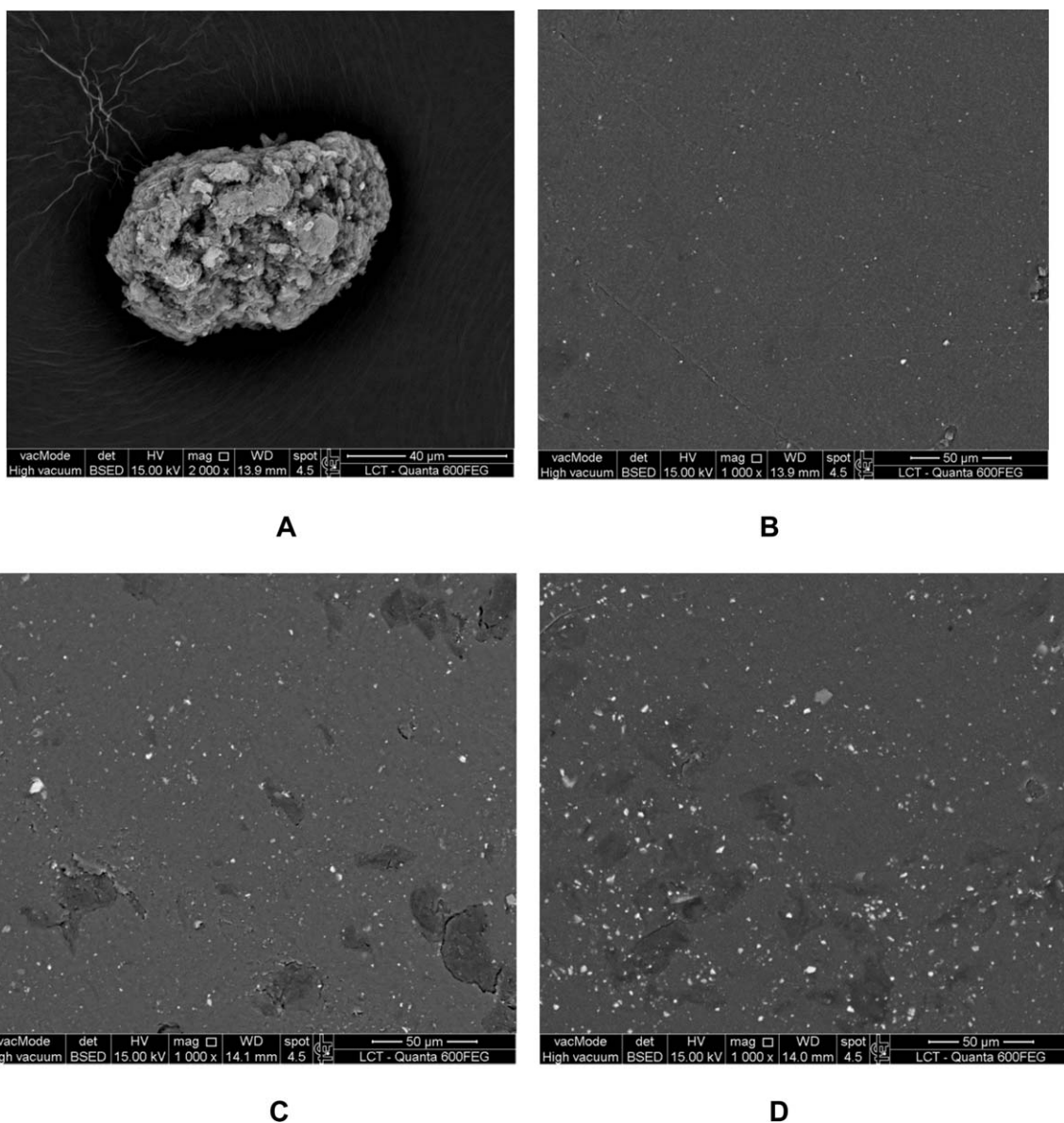


Figure 1. SEM images (with 1000 × magnification) concerning to the MMT Cloisite® 10A pure (A); Group 1 (50 wt % MMT) (B); Group 2 (60 wt % MMT) (C); Group 3 (70 wt % MMT) (D).

For shrinkage ($p = 0.004$), ANOVA showed that the interaction between two factors was significant ($p < 0.0001$) and the Tukey's test, showed five different subgroups. The polymerization shrinkage values of experimental composites filled with MMT nano particle, ranged from 1.9 to 0.17% and the groups added with silica, from 2.72 to 0.51%.

Differential Scanning Calorimetry (DSC)

It was possible to monitor whether the specimens previously polymerized were properly cured/converted by comparison of the behavior for pairs of specimens from the same group, one previously photo polymerized in TMA via UV and another nonpolymerized.

A clear distinction in thermal behavior was observed, as the nonpolymerized specimens displayed an exothermic reaction (100–130 °C), that is, polymerization occurred through thermal stimulus. The

cured perfil, previously polymerized specimens, presented none event in the expected polymerization range (100–170 °C).

In Figure 4 an example of comparison between a pair of specimens from group 1 (50 wt % MMT) is presented; specimen A is nonpolymerized and specimen B was previously polymerized by TMA.

Knoop Micro Hardness

The Knoop micro hardness values of the experimental composites can be found in Table III. For micro hardness ($p = 0.004$), ANOVA reported that the interaction between the two factors was significant ($p < 0.0001$) and Tukey's test showed three different subgroups. The micro hardness values were similar, comparing the groups filled with MMT nano particle and silica, except the group added with 70% of MMT that was statistically higher. Knoop micro hardness values of experimental

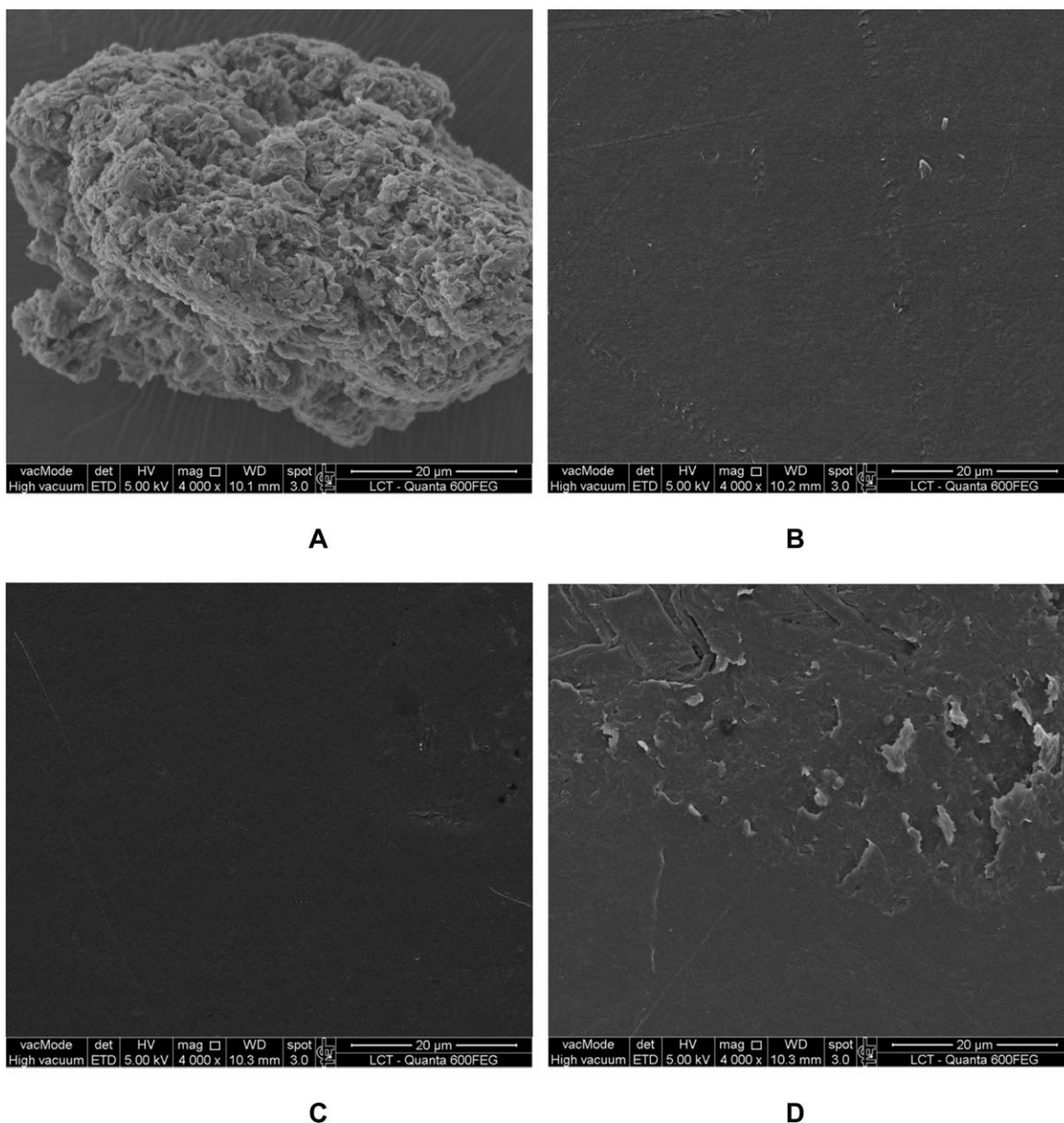


Figure 2. SEM images (with the 4000 \times magnification) concerning to the MMT Cloisite[®] 10A pure (A); group 1 (50 wt % MMT) (B); group 2 (60 wt % MMT) (C); group 3 (70 wt % MMT) (D).

composites filled with MMT nano particle, ranged from 12.50 to 19.40 and the groups added with silica, from 12.27 to 15.47.

X-ray Diffraction (XRD)

The XRD patterns of the MMT Cloisite[®] 10A nanoparticle can be seen in Figure 5, as well as its interlamellar distance, " d_{001} " = 1.93 nm, and the values of " d " for the experimental composites.

From Figure 5, it was observed the presence of two distinct peaks. One concerning clay-polymer intercalation, with interlamellar distance " d " ranging from " d " = 3.51 nm to " d " = 3.56 nm, and the second in the same region of pure clay. Part of the filler suffered exfoliation, while another part undergoes intercalation, which explains the presence of the peaks attributed to " d " at around 3.53 nm.

Furthermore, there seems to be another part of clay that remains in agglomerated form, identifiable by the peak in the same region of pure clay d = 1.95 nm, credited as excess clay, i.e., a certain amount of clay had no intercalation with the polymer, leaving its lamellar structure almost unchanged.

Degree of Conversion (DC)

The results of Degree of Conversion are reported in Table IV. For degree of conversion, ANOVA showed that the interaction between factors type and amount was not significant (p = 0.762), as for the factor amount (p = 0.430). The factor type was statistically significant (p < 0.0001).

The Tukey's test showed that the Degree of Conversion was higher for MMT than silica. Groups of experimental composites filled with MMT nanoparticle, showed degree of conversion

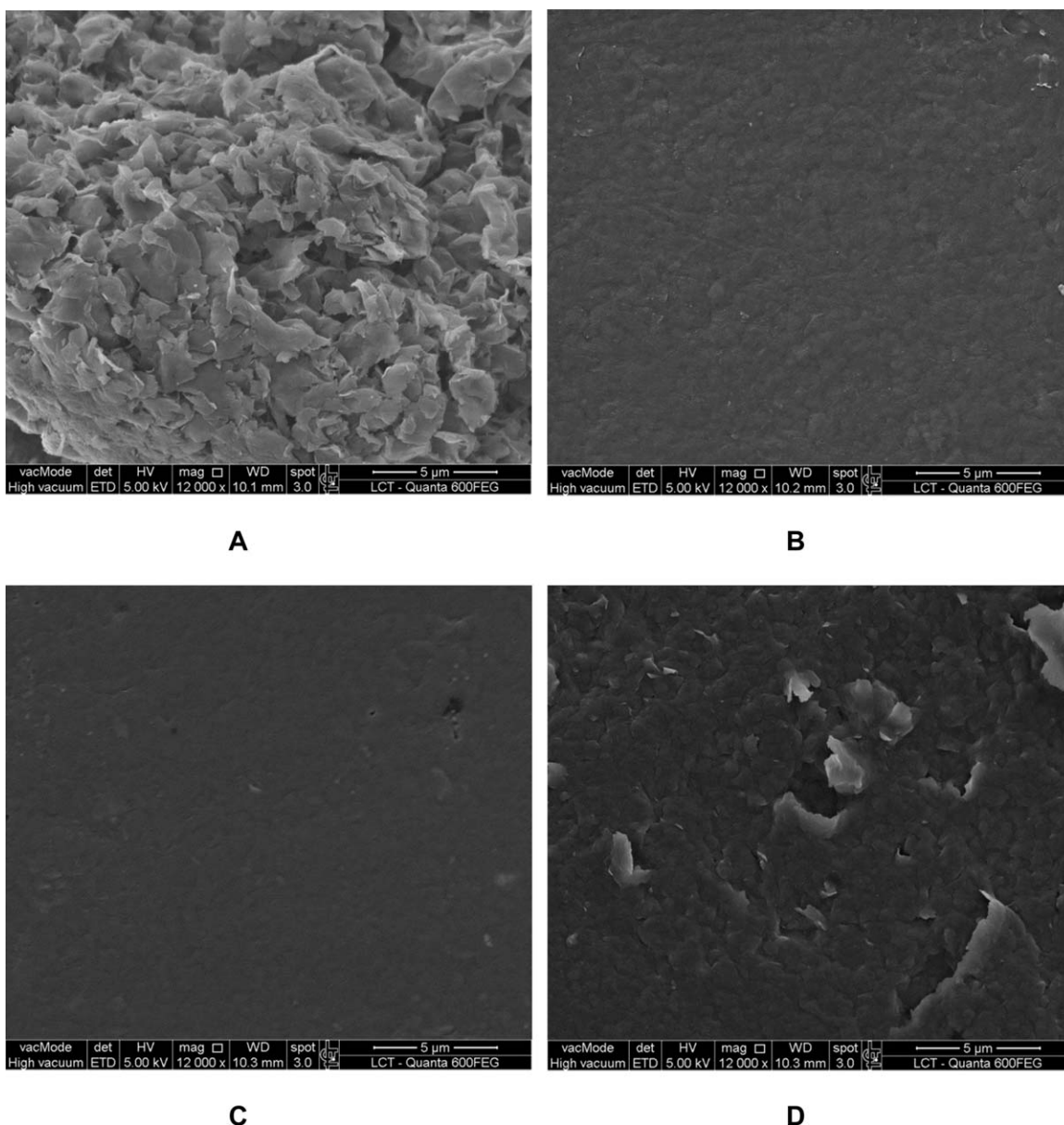


Figure 3. SEM images (with the 12,000 \times magnification) concerning to the MMT Cloisite[®] 10A pure (A); group 1 (50 wt % MMT) (B); group 2 (60 wt % MMT) (C); group 3 (70 wt % MMT) (D).

from 50 to 53%, and the groups added with silanized silica, from 14 to 18%.

Flexural Strength/Elastic Modulus

The results for Flexural Strength and Elastic Modulus can be observed in Table V. For Flexural Strength the interaction between factors type and amount was not significant ($p = 0.121$), as for the factor amount ($p = 0.624$). The factor type was statistically significant ($p < 0.0001$). For Elastic Modulus the interaction between the two factors was significant ($p < 0.0001$).

The Tukey's test showed that the Flexural Strength was lower for MMT than for silica, and the Elastic Modulus was higher when 70 wt % of MMT was used. The others groups, was statistically similar. Flexural strength of the groups filled with MMT

ranged from 22.15 to 25.77 MPa and in the groups filled with silica, ranged from 65.88 to 57.73 MPa, which showed a different behavior between the types of filler. Elastic modulus of the groups filled with MMT ranged from 1.70 to 2.63 GPa and in the groups filled with silica, from 1.49 to 1.67 GPa.

Transmission Electron Microscopy (TEM)

Intercalation phenomena observed by X-ray Diffraction was confirmed in the Transmission Electron Microscopy images (Figure 6). TEM showed predominantly intercalation effect of MMT nanoparticle in relation to polymeric matrix for all groups filled with MMT, in other words, was found that polymeric matrix entered between the silicate layers. Thus, TEM images corroborate with the results obtained by XRD.

Table II. Means (Standard Deviations) for Polymerization Shrinkage (%)

Filler		Shrinkage polymerization (%)
Type	% in weight	
MMT	50	1.90 (0.13) B
	60	0.52 (0.17) D
	70	0.17 (0.05) E
Silica	50	2.72 (0.37) A
	60	1.10 (0.25) C
	70	0.51 (0.13) D

In the same column, means followed by the same letter are statistically similar ($p > 0.05$).

DISCUSSION

In spite of the limitation involved in the manual mixing and manipulation of the experimental composites, the dispersion of the nanoparticles and absence of voids, observed by SEM images, were noticeable for all the analyzed groups. The best clay distribution can be seen for samples containing 50% MMT Cloisite® 10A. Furthermore, small clusters of nanoparticles were observed, demonstrating that MMT has a tendency for clustering. These results match previous studies in which the authors observed the formation of a great number of tactoids in experimental dental composites containing above 16 wt % MMT. The authors suggested that this clustering occurs during filler mixing.¹²

Regarding Thermo-Mechanical Analyses (shrinkage polymerization) as expected, for experimental composites containing silanized silica, a typical behavior of inert particle filler reinforced polymers was observed: there is a direct correlation between the increase in inorganic filler and polymerization shrinkage reduction, as demonstrated by the linear decrease in shrinkage ($R^2 = 0.9972$). Experimental composites containing 50 wt % of MMT nanoparticles displayed values close to those obtained with the same amount of silanized silica inorganic filler. However, a greater reduction in polymerization shrinkage was

Table III. Means (Standard Deviations) for Micro Hardness Knoop

Filler		Micro hardness knoop
Type	% in weight	
MMT	50	12.50 (0.31) C
	60	13.87 (0.50) BC
	70	19.40 (0.53) A
Silica	50	12.27 (0.81) C
	60	13.20 (1.20) C
	70	15.47 (1.10) B

In the same column, means followed by the same letter are statistically similar ($p > 0.05$).

observed for 60 and 70 wt % of inorganic filler, which indicates a different form of matrix/filler interaction ($R^2 = 0.9319$).

Lower polymerization shrinkage values displayed by the all groups containing MMT compared to silanized silica groups, can be attributed to the interaction between the polymer matrix and the mineral clay nanoparticles. It may relate to the fact that the interface between the polymer matrix and the clay developed certain properties due to the increase in surface area and new characteristics were obtained. The property of certain clay minerals of absorbing organic molecules causes their lamellae to grow apart and disperse in the polymer matrix, increasing the volume occupied by the material. Some authors hypothesize that this expansive nature is capable of reducing the magnitude of the polymerization shrinkage and residual stresses in these composites.^{8,9} According to the results presented, as well as in previous work,¹³ DSC analysis confirms the effectiveness of TMA for curing/conversion of the experimental composites.

The reduction of polymerization shrinkage in experimental composites containing Cloisite® 30B MMT was observed in another study.¹³ According to the authors, the chemical affinity between the (BisGMA/TEGDMA based) polymer matrix and the clay mineral Cloisite® 30B nanoparticle (made organophilic through surface treatment with Methyl-Tallow-bis-2-hydroxyethyl

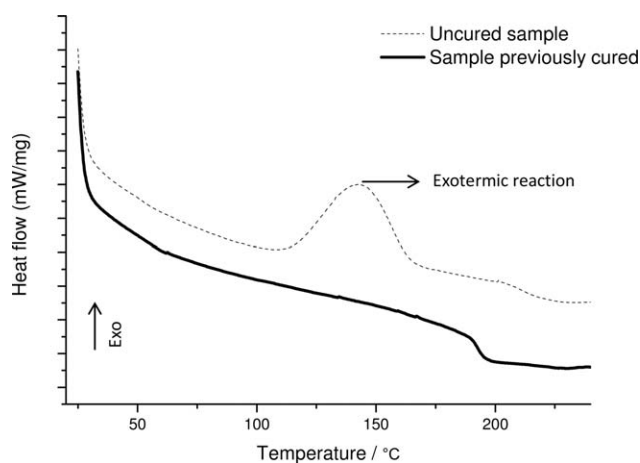


Figure 4. Comparison by DSC of Group 1 (50 wt % MMT). (A) uncured sample; (B) sample previously polymerized by TMA analysis.

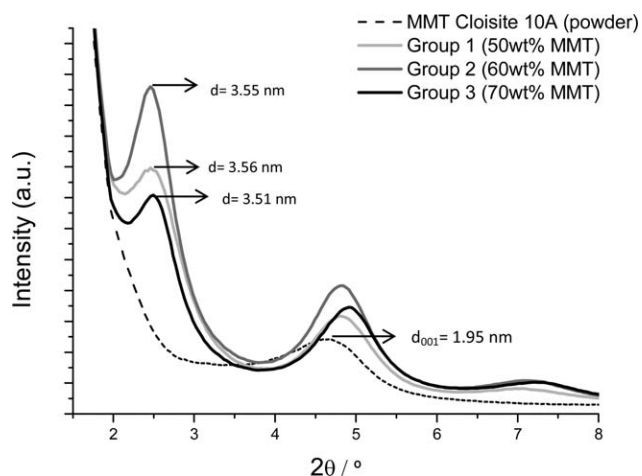


Figure 5. XRD pattern of MMT pure (powder), Groups 1 (50 wt % MMT), 2 (60 wt % MMT), and 3 (70 wt % MMT).

Table IV. Means (Standard Deviations) for Degree of Conversion (%)

Type	Filler		Degree of conversion (%)
	% in weight		
MMT	50		53 (4) A
	60		52 (6) A
	70		50 (10)A
Silica	50		15 (1) B
	60		14 (2) B
	70		18 (3) B

In the same column, means followed by the same letter are statistically similar ($p > 0.05$).

- MT2EtOH - quaternary ammonium salt) were determinant with regards to polymerization shrinkage reduction.

As observed in the present study, the experimental groups filled with silanized silica showed higher polymerization shrinkage values, compared to group added with MMT, even presenting low degree of conversion values. According to Du and Zang (2008),²⁴ composites filled with silanized silica showed a decrease with the increasing filler content and this may be related to the increases of the viscosity of composites, the mobility and reactivity restriction of the amine reactants, which affects the vinyl conversion. In addition, filler concentration, size, and refractive index that may interfere in the dispersion of light and thus in the depth of cure and degree of conversion.²⁵ Regarding groups filled with MMT nanoparticle, DC was not affected by the type of interaction between the MMT and a polymer matrix, even at high concentration of filler. In other words, there was no alteration in the scission of carbon double bonds responsible for the monomer conversion.

The phenomenon of MMT nanoparticle intercalation in a BisGMA/TEGDMA based polymeric matrix observed in the experimental composites by XRD and TEM images, can justify the improved results observed in the polymerization shrinkage analysis. According to Campos *et al.* (2014)¹³ the intercalation of Cloisite® 30B nanoparticle in dimethylacrylate-based polymeric matrix resulted in a best performance with regards to polymerization shrinkage when compared to composites con-

Table V. Means (Standard Deviations) for Flexural Strength (MPa) and Elastic Modulus (GPa)

Type	Filler		Flexural strength (MPa)	Flexural modulus (GPa)
	% in weight			
MMT	50		22.15 (1.67) B	1.70 (0.38) B
	60		24.09 (2.93) B	1.64 (0.40) B
	70		25.77 (5.87) B	2.63 (0.33) A
Silica	50		65.88 (11.46) A	1.49 (0.24) B
	60		64.61 (12.23) A	1.50 (0.37) B
	70		57.73 (13.38) A	1.67 (0.24) B

In the same column, means followed by the same letter are statistically similar ($p > 0.05$).

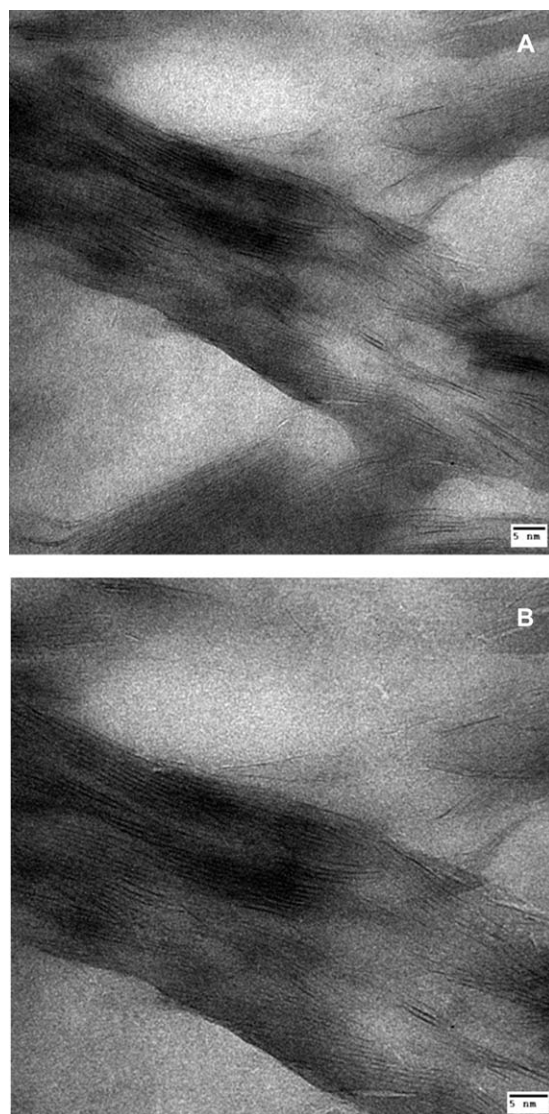


Figure 6. TEM images of experimental composites added with 60% of MMT nanoparticle. (A) with 250.000 \times magnification; (B) with 300.000 \times magnification.

taining silanized silica, which acts as inert filler. Some authors believe that this expansion could minimize polymerization shrinkage and ensuing residual stresses in these composites.^{8,9}

Intimate clay-polymer interaction is desirable, because if clay agglomerates remain dispersed in the polymeric matrix, it will act as conventional filler, even if it has nanometric dimension. This is possible due to the large amount of clay added to the composite and corroborates the appearance of tactoids seen for clay concentration above 16% previously reported.¹² If clay intercalates and/or exfoliates during processing, however, it will allow the constitution of a nanocomposite, promoting reinforcement characteristics that cannot be achieved.^{26,27} However, the agglomerates can act as stress raisers, reducing the failure strength of the material.²⁸ The agglomeration, observed by SEM images, also reduces the intercalation effect, which further compromises the mechanical properties.²⁹

MMT nanoparticles agglomeration was the primary reason for a decrease in the Flexural Strength of the experimental composites, however the agglomerate was strong enough to significantly increase the Elastic Modulus and Micro hardness Knoop at concentration of 70 wt %. These results can be related to the high stiffness and high modulus, characteristic of these lamellar silicate nanoparticles.³⁰ Nanometric particles hold higher contact surfaces with the matrix which may contribute to this increase.²⁷

Regarding Flexural Strength, composites filled with MMT nanoparticle and silica showed different behaviors (Table V). Experimental composites filled with silica showed a decreased of mechanical properties, as filler concentration increased. These results corroborate with a previous study in which the authors observed decrease in flexural strength when the silica concentration reached 50% content.³¹ According with authors, the silica filler concentration played a critical role in determining the experimental composites mechanical properties.

In the experimental composites filled with MMT, the low values of the Flexural Strength, compared to composites filled with silica, may be related to the cluster and cracks formation. Clay aggregation, cracks, fissures, and scale-like layers are noticeable in samples with more than 60 wt % of clay concentration.¹³ These cracks may be responsible for additional shrinking reduction due to the polymeric chains immobilized in-between clay layers. Nevertheless, a drawback effect of the crack formation could be the reduction in mechanical properties, hindering the benefits of clay in nanocomposites.²⁹ In addition, at high filler concentration it was observed the appearance of tactoids and functionalization of MMT nanoparticle did not promote a strong interface adhesion between polymeric matrix and filler. In order to adjust the mechanical properties, it would be convenient to promote the concentration optimization of MMT nanoparticles.^{28–32}

CONCLUSIONS

TMA results showed that experimental composites filled with MMT nanoparticle present statistically lower polymerization shrinkage values and statistically high degree of conversion in all formulations tested, when compared to composites filled with silanized silica, and it could be related to the type of interaction (intercalation effect) between MMT/polymeric matrix, as observed in XRD/TEM analyses. DSC analyses allow the verification that photo polymerization and curing of the polymer were properly achieved for composites containing both fillers. Regarding Micro Hardness Knoop and Elastic Modulus, experimental composites filled with both types, showed similar values, except for group filled with 70 wt % of MMT, that statistically showed the highest values that could be related to the high modulus of the MMT nanoparticles. For Flexural Strength, groups filled with MMT nanoparticle showed statistically lower values for all concentration tested. At high filler concentration it was observed the appearance of tactoids and functionalization of MMT nanoparticle did not promote a strong interface adhesion between polymeric matrix and filler. In order to adjust the

mechanical properties, it would be convenient to promote the concentration optimization of MMT nanoparticles.

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