

Polymerization shrinkage evaluation in experimental dental composite filled with montmorillonite nanoparticles

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Abstract This study aimed to develop experimental dental restorative composites by the addition of montmorillonite (MMT) nanoparticles in a polymeric matrix-based BisGMA/TEGDMA, to assess the possibility of a different dimensional behavior during the photo-polymerization. The characterization of experimental composites was established with the following analyses: thermal–mechanical analysis (TMA), X-ray diffraction (XRD) and transmission electron microscopy. Data for TMA were analyzed using one-way ANOVA and Tukey test ($p < 0.05$). It was observed that the experimental composites filled with MMT nanoparticle showed statistically similar polymerization shrinkage values (by TMA analysis) in the concentration of 30% and statistically lower polymerization shrinkage values in the concentration of 50%, compared to composites filled with barium glass (BG—control groups). These results may be related to the interaction polymeric matrix/MMT nanoparticles and the formation of nanocomposites, observed by XRD and TEM analyses.

Keywords Thermal–mechanical analysis (TMA) · Shrinkage polymerization · Nanoparticles · Montmorillonite (MMT)

Introduction

The composite resins used by dentists in adhesive dental restorations are versatile materials which use is growing continuously since their introduction on dental market about five decades ago [1, 2]. Due to its esthetics and ability to direct technique, the composite resin is the main material for dental restorations [3]. Improvements in the polymeric matrix-based BisGMA/TEGDMA and in the filler particles have increased significantly the properties of these composites materials [4].

The addition of MMT clay mineral nanoparticles in polymeric matrix has been extensively studied, but its use initially caught the attention of the plastics industry due to the improvement in optical, thermal and mechanical properties [5]. According to previous studies, the possibility of incorporation of MMT nanoparticles in restorative dental composites has the ability to reduce the polymerization shrinkage and residual stress [6–8] improved lifetime performance, abrasion resistance and resistance to solvent absorption [9].

According to Alexandre and Dubois [10], nanoclays have a nanometric lamellar structure and are composed of thin layers spaced by alkaline cations that interact through van der Waals forces with each other and with organic molecules. These cations balance the isomorphous substitutions of Al^{+3} atoms by Mg^{+2} or Fe^{+2} atoms, or Mg^{+2} atoms by Li^{+} in the octahedral sheets [10]. These substitutions cause distortions in the lamellar structures, generating a negative charge excess in the layers of the clays. To promote greater compatibility with organic polymers, the clays can be organophilized by exchanging of the cationic surfactants such as alkylammonium or alkylphosphonium [11].

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This study aimed to develop experimental restorative dental composites by the addition of MMT nanoparticles in a polymeric matrix-based BisGMA/TEGDMA, to assess the possibility of a different dimensional behavior during the photo-polymerization.

Materials and methods

Formulation of experimental composite

Four groups of experimental composites were prepared according to the type and concentration (in percent) of inorganic filler. In Table 1 are the formulations and the identification of all experimental composites groups used in this study:

Mineral clay MMT Cloisite® 20A used in this study, according to the manufacturer, was previously made organophilic through surface modification by hydrogenated quaternary ammonium tallow (2M2HT), in the concentration of 90 meq/100 g⁻¹ clay, chloride anion, where “Tallow” represents an alkyl group (with approximately 65% of C18; 30% C16; and 5% C14). Cloisite® 20A MMT has $d_{001} = 1.92$ nm as the main X-ray diffraction initial peak, which also indicates its interlamellar spacing. According to Campos et al. [7], MMT nanoparticles comprise a lamellar structure (composed of stacking layers) with thickness of ~ 1 nm.

Thermomechanical analysis (TMA)

The TMA/SDTA840 from Mettler Toledo measured dimensional changes (shrinkage polymerization) of the experimental composites during the cure process ($n = 10$ of diameter = 10 mm) at constant temperature of 25 °C, under quartz contraction probe on static mode, operating simultaneously to the photo-polymerization apparatus (Radii-cal/SDI, Australia) under photo-excitation of the sample at 468 nm wavelength (18 J cm⁻²). During the photo-polymerization process (3 min), the TMA measured the main volumetric changes of the samples. According to

previous studies, this methodology measured the polymerization shrinkage on real time, with a precision of 0.1 μm along a single axis (z), making it a simple, accurate and reliable measurement [7, 9].

X-ray diffraction (DRX)

The interlayer spacing of experimental composites filled with MMT nanoparticles was calculated according to the Bragg's equation: $n \lambda = 2d \sin \Theta$, 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 (TEM)

By transmission electron microscopy, it was possible to observe, through images, the interaction of the polymeric matrix in relation to the MMT nanoparticles, thus enabling complement the data obtained by X-ray diffraction. The specimens for TEM analyses were ultramicrotome to 60-nm-thick slices, 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 analysis

Data for polymerization shrinkage (TMA) were analyzed using one-way ANOVA and Tukey test. For all tests, the global significance level was 5%.

Results and discussion

Thermomechanical analysis (TMA)

Polymerization shrinkage results of the experimental composites filled with MMT nanoparticles and silanized silica (control groups) are described in Table 2.

The experimental composites filled with 30% of MMT nanoparticles showed statistically similar shrinkage polymerization values compared to the experimental composites added with barium glass (control group). However, when the filler concentration increased to 50%, it was observed that the shrinkage polymerization of the composites filled with MMT nanoparticles remained lower, revealing that the inorganic filler type used in this study showed influence on polymerization shrinkage by the mechanical behavior of the experimental composites.

It may relate to the fact that the interface adhesion between the polymer matrix and the clay developed certain

Table 1 Materials used in experimental composite formulations

Mass/mg	Group 1	Group 2	Group 3	Group 4
BisGMA	348	248	348	248
TEGDMA	348	248	348	248
Camphorquinone	2	2	2	2
DMAEMA	2		2	2
MMT 20A	300	500	–	–
Barium glass	–	–	300	500
Total mass	1000	1000	1000	1000

Table 2 Shrinkage polymerization results by TMA methodology

Group	Shrinkage/%
1 (30% MMT)	2.36 ± 0.32 A
2 (50% MMT)	0.44 ± 0.18 C
3 (30% BG)	2.73 ± 0.48 A
4 (50% BG)	1.01 ± 0.48 B

Means (standard deviation) for shrinkage polymerization (%)

Values followed by the same letter presented no difference statistically significant ($p < 0.05$)

properties due to the increase in surface area where new characteristics were obtained. According to some authors, the ability of MMT clays nanoparticles to absorb organic molecules increases lamellae distances from each other, developing an additional volume within the material. The authors' hypothesis was that expansive nature of the clay could reduce the polymerization shrinkage and residual stress of the composites [7, 8].

TMA analysis is a highly sensitive and reliable method for evaluating the coefficient of thermal expansion and contraction (including shrinkage polymerization) for different types of materials [12–14].

X-ray diffraction (DRX)

Figure 1 shows the XRD patterns of MMT nanoparticles pure (Cloisite® 20A) and the XRD patterns of experimental groups added with MMT nanoparticles.

Through the XRD pattern, it was observed the peak $d_{001} = 3.48$ nm, relative to pure MMT nanoparticle, and the peaks $d = 3.57$ nm (50% MMT) and $d = 3.77$ nm (30% MMT) corresponding to the experimental composites filled with MMT. These results showed a displacement of

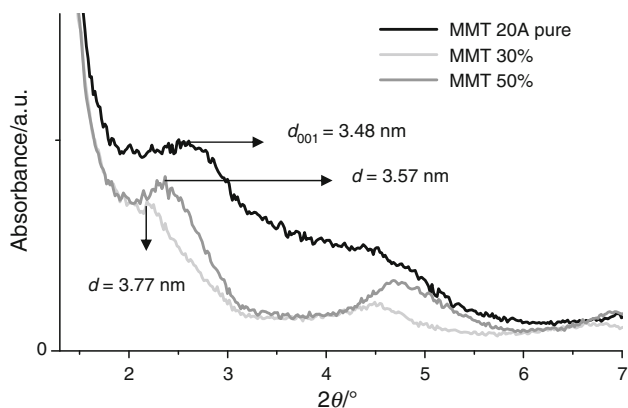


Fig. 1 XRD patterns of MMT nanoparticle pure and experimental composite groups filled with 30 and 50% of MMT

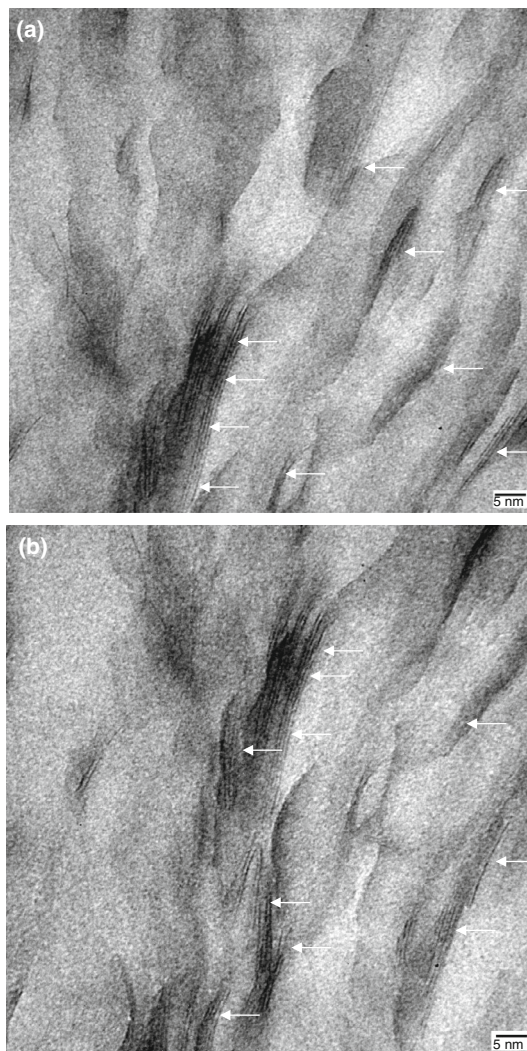


Fig. 2 TEM images of experimental composites added with 30% of MMT nanoparticle (a, b). Arrows indicate the intercalation of nanoparticles in relation to the polymeric matrix-based BisGMA/TEGDMA

the basal interplanar distance. The displacement of the original “ d_{001} ” peak for smaller angles, or an increase in the interlayer space, characterized the entry of the polymer into the clay layers, in other words, the intercalation phenomena.

This type of interaction (intercalation) filler–matrix being stronger and more stable than the interaction that occurs with barium glass can result in an increase in properties, as evidenced by TMA results. MMT nanoparticle just dispersed in a polymeric matrix will act as conventional filler, but if clay intercalated and exfoliated in the polymer matrix during processing, it could be able to act as a nanocomposite, promoting better characteristics of reinforcement [15].

Transmission electron microscopy (TEM)

Transmission electron microscopy images in Fig. 2 report the MMT nanoparticle intercalation phenomenon in relation to the polymer matrix, thus corroborating with the results obtained by X-ray diffraction and previous studies [7, 16].

Conclusion

Based on TMA results, it was concluded that the experimental composites filled with MMT nanoparticle showed statistically similar polymerization shrinkage values in the concentration of 30%, in comparison with the control groups; however, when the filler concentration increased to 50%, the experimental composite filled with MMT nanoparticles showed statistically lower shrinkage polymerization values. These findings revealed the influence of MMT nanoparticles in the polymerization shrinkage results and owing to the intercalation effect of nanoparticles in polymeric matrix, as observed in XRD/TEM analyses.

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