

EFFECT OF MMT NANOPARTICLE CLAY ON FLEXURAL PROPERTIES OF POLYMER BASED BISGMA/TEGDMA RESIN

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Abstract

The objective of this study is to evaluate the (strength and modulus) and degree of conversion of dimethacrylate resin containing different amounts of Montmorillonite (MMT) Cloisite 20A nanoclay as filler. Eight formulations of polymer based BisGMA/TEGDMA (four with MMT and another four with barium glass (BG) as filler) at concentration of 20, 30, 40 and 50% by weight were studied. As control, a series of composites containing BG particles were also tested. The flexural strength data was analyzed using Kruskal-Wallis and Tukey's tests. The addition of MMT nanoparticles in a BisGMA / TEGDMA resin matrix resulted in similar degree of conversion and higher elastic modulus values compared to the groups filled with BG. The decrease in the resistance value with increasing concentration of MMT may be due to the formation of agglomerates (clusters) that decreases the reinforcement efficiency.

Introduction

Dental reparation based in composite resin replaced metal amalgams due to its advantages, as the possibility of performing conservative cavity preparation and superior aesthetics results [1]. However, this material suffers a volume contraction during polymerization, leading to residual stresses, postoperative soreness, microcracks formation between the tooth and the restoration, resin detachment from the remaining tooth and even cusp deflection may occur [2-3].

Structural changes caused by multifunctional methacrylate monomers introduction and higher inorganic filler additions produce more wear-resistant materials with higher elastic modulus. Up to 75-85 wt% of filler particles (such as quartz, silica and barium glass) may be added to the resin matrix to improve mechanical properties and reduce polymerization shrinkage to less than 3.0 % [4-5].

Polymers reinforced with different amounts of mineral clays have been studied, with enticing results in the plastic industry, due to the improvement of optical, thermal and mechanical properties [6-7]. Clays are formed by lamellar structure in which their layers present thickness of approximately 1nm, but length and breadth ranging between 100 and 1000 nm [7].

Many types of clay (such as Montmorillonite - MMT) have the capacity to absorb organic molecules in-between their layers. This level of interaction hinders in polymer-clay composites shrinkage due to changes in overall free volume, since clay lamellae can grow apart and disperse throughout the polymeric matrix. Some authors claim there was a polymerization shrinkage reduction of a BisGMA/TEGDMA based composite after the introduction of layered silicate [8-9]. The introduction of these mineral clays in the composite expected to reduce polymerization shrinkage and residual stresses [10-12].

Therefore, the aim of this study was to evaluate the degree of conversion and flexural properties (strength and modulus) of dimethylacrylate resin composites containing different amounts of MMT nanoparticles. Composites containing similar quantities of silanized barium glass particles (BG) were produced and tested as control groups. 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

Two series of experimental composites were formulated, both with the same resin matrix (BisGMA:TEGDMA) and 20, 30, 40 or 50 wt % of filler. The photo initiator and tertiary amine corresponded to 0.2 wt% 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 μ m).

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[®] 20A MMT, manufactured by Southern Clay Products, USA; Silanized Barium Glass, provided by FGM, BRA. Table 1 show the materials used in composite formulation.

Mineral clay Cloisite[®] 20A MMT used in this study, according to the manufacturer, was previously organophilised through surface modification by dimethyl dehydrogenated tallow (2M2HT) quaternary ammonium chlorine, with a concentration of 95 meq per 100g⁻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[®] 20A MMT has $d_{001} = 24.2 \text{ \AA}$ as the main X-Ray diffraction initial peak, which also indicates its interlamellar spacing.

Table 1: Formulations of experimental composites groups.

| Mass (mg) | | | | | | | | |
|-------------------|---------|---------|---------|---------|---------|---------|---------|---------|
| | Group 1 | Group 2 | Group 3 | Group 4 | Group 5 | Group 6 | Group 7 | Group 8 |
| BisGMA | 398 | 348 | 298 | 248 | 398 | 348 | 298 | 248 |
| TEGDMA | 398 | 348 | 298 | 248 | 398 | 348 | 298 | 248 |
| Camphor. | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| DMAEMA | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| MMT 20A | 200 | 300 | 400 | 500 | - | - | - | - |
| BG | - | - | - | - | 200 | 300 | 400 | 500 |
| Total Mass | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |

Methods

Degree of Conversion (DC)

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 frame (h=0.8mm, Ø=7.0mm) 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 seconds, using a LED curing light (Kondordeck's Aigh-7A LED, at 470 nm wavelength, commonly used to the dental composite cure). Degree of conversion was determined by assessing the change in area of the absorbance peak at 1665 cm⁻¹, corresponding to the first overtone of the methacrylate vinyl stretch in relation to the uncured material [13].

Flexural Modulus and Flexural Strength

Specimens 10x2x1 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, 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 x displacement curve, flexural modulus was calculated according to the equation 1 [13]:

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

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 the equation 2 [13]:

$$\sigma = \frac{3FL}{2bh^2} \quad (\text{equation 2})$$

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).

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 “d₀₀₁” peak is characteristic for the nanoclay. MMT Cloisite[®] 20A has “d₀₀₁” = 2.42 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 K α radiation ($\lambda=1.54186$ Å, 45 kV, 40A) at room temperature, the diffraction were scanned from 1.17° to 40° in 2 θ range with 0.03° step at step/time 100s. The interlamellar spacing was calculated according to Bragg’s equation: $n \lambda = 2d_{hkl} \sin \theta$ (equation 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.

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 and Discussion

Means and standard deviations for degree of conversion (DC) shown in Table 2. Composites containing silanized barium glass and MMT nanoparticles showed no statistically significant among filler contents. For a similar filler level, DC was statistically similar for both types of filler, except for the concentration of 40 wt% that resulted in higher DC for the MMT composite. According to the results obtained in this study (Table 2) it was observed similar degree of conversion for all concentrations in composites with BG.

The absence of statistical difference among different filler content has been reported in a previous study [5]. At concentrations of 20, 30 and 40% in weight, the composites added with MMT were statistically similar. The only exception corresponded to the group containing 50 wt% 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 may interfere in the dispersion of light and thus in the depth of cure and degree of conversion [14].

For given filler level, the degree of conversion of the groups using BG and MMT (Table 2) was statistically similar, except at a concentration of 40 wt%. 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 [8-9].

Table 2: Means (with standard deviation in parentheses) for degree of conversion (%). 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.

| Filler content (wt%) | Degree of Conversion (%) | |
|----------------------|--------------------------|---------------|
| | MMT 20A | Barium Glass |
| 20 | 69.9 (1.9) Aa | 65.0 (6.7) Aa |
| 30 | 71.2 (4.6) Aa | 65.6 (6.0) Aa |
| 40 | 71.9 (3.2) Aa | 63.1 (6.3) Ab |
| 50 | 65.6 (4.8)Ba | 63.4 (4.9) Aa |

Regarding flexural properties (Table 3), the interaction between filler type and content was significant for both strength and modulus ($p=0.018$). Flexural modulus decreased with filler content for the composites containing MMT nanoparticles. Among composites containing BG an increase in modulus was observed between 30 and 50 wt%. Regarding filler types, the groups with MMT nanoparticles showed higher flexural modulus, except at 50 wt% where both fillers displayed similar modulus.

Composites containing BG as filler showed an increase in the elastic modulus as the filler concentration increased (Table 3), in accordance with previous studies [15]. The increase in elastic modulus values due to an increase in filler generally follows the rule of mixture [16]. Composites filled with BG showed elastic modulus values similar to those reported in other studies [5]. Meanwhile the experimental composites filled with MMT had higher elastic modulus than the BG groups, except for the materials with 50 wt%, which were statistically similar. This higher elastic modulus found with the MTT composites values may be related to high stiffness and high modulus of the lamellar silicate particles [17]. In addition, the nanoparticles have greater contact surface with the organic phase, which can result in increased mechanical properties [6].

The composite containing 50 wt% MMT showed the lowest elastic modulus values compared to the others MTT-filled materials. The agglomeration of MMT nanoparticles in the polymer matrix, may have contributed to this result. 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 [8]. After 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 [18-19].

Among the groups filled with MMT, the flexural strength results (Table 3) were similar at 20% and 30% (v/v). However, lower value was achieved at 40 and 50 wt%. With regard to the addition of BG, a relevant difference was observed for the group containing 20 wt%. By comparing the two types of filler, the groups filled with MMT

nanoparticle showed a value statistically higher in relation to the groups added with BG at a concentration of 20 and 30 wt%, while are observed lower values at concentrations of 40 and 50 wt%.

Table 3: Means (with standard deviation in parentheses) for elastic modulus (GPa) and flexural strength (MPa). 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.

| Filler content (wt%) | Flexural modulus (GPa) | | Flexural strength (MPa) | |
|----------------------|------------------------|---------------|-------------------------|----------------|
| | MMT | BG | MMT | BG |
| 20 | 3.09 (0.48) Aa | 0.35 (0.26)Bb | 69.1 (8.1)Aa | 32.0 (13.1)Bb |
| 30 | 2.47 (0.51) Aa | 0.49 (0.18)Bb | 73.07(9.2) Aa | 55.9 (18.1)Aba |
| 40 | 1.81 (0.65) Ba | 1.02 (0.5)ABb | 38.4 (5.2) Bb | 66.7 (25.5)Aa |
| 50 | 1.68 (0.74) Ba | 1.47 (0.55)Ab | 23.9 (6.1) Bb | 65.2 (18.0)Aa |

Regarding flexural strength, the composites filled with MMT nanoparticle and BG showed different behaviors (Table 3). It was observed that for the MMT groups that strength decreased as filler concentration increased, while for the BG groups the opposite behavior was found, in accordance with previous studies [5]. At high MMT levels, the formation of agglomerates (clusters) decreases the reinforcement efficiency. According to Hussain (et al. 2007) [17], the particle agglomeration (MMT) is the primary reason for a decrease in the strength of the material, even if the agglomerate is strong enough to significantly increase the elastic. Flexural strength decreased because functionalization of MTT was not sufficient to form adherent strong interface between filler and polymeric matrix. Thereby, they act as defects within the composites that may act as a 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 mechanical properties [18].

Diffraction patterns of the MMT powder, as well as the MMT nanoparticles added to the resin matrix are shown in Figure 1. The diffraction peak interlamellar spacing of the "pure" MMT was calculated as $d_{001} = 3.48$ nm. The "d" values for the MMT filled on the polymeric matrix were: $d = 3.77$ nm for the composites containing 20 wt% MMT; $d = 3.68$ nm for the composites containing 30 wt% MMT; $d = 3.58$ nm for the composites containing 40 wt% MMT and $d = 3.57$ nm for the composites containing 50 wt% MMT. The displacement of 2 θ peak related to the interlamellar spacing " d_{001} " for smaller angles was observed. That displacement of the initial " d_{001} " peak for smaller angles for both groups characterized the entry of the polymer into the clay layers in intercalation form. XRD patterns (Figure 1) showed predominantly intercalation effect of MMT nanoparticle in relation to polymeric matrix for all groups, as previously observed in other studies [8-9]. 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 [7]. 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. All MMT groups' concentration, the flexural modulus values were statistically higher than the composites added with BG.

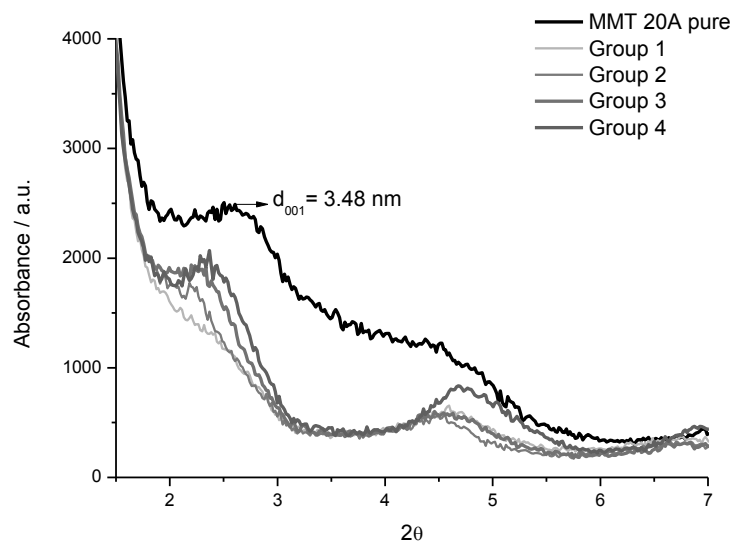


Figure 1: XRD patterns of MMT 20A pure and experimental composites groups.

Conclusion

Based on the results obtained in this study, it can be concluded: despite fillers MMT and BG interact with polymer matrix based BisGMA/ TEGDMA in a distinct manner, 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 analysis; regarding flexural strength, only MMT group's with low concentration showed the highest value if compared to composites added with BG. The decrease in the resistance value with increasing concentration of MMT may be due to the formation of agglomerates (clusters) that decreases the reinforcement efficiency.

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