

# **INFLUENCE OF RADIATION ON THE THERMAL AND MECHANICAL PROPERTIES OF BISGMA / TEGDMA BASED NANOCOMPOSITES USING PRE-IRRADIATED MMT NANOPARTICLES AS FILLER**

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## **ABSTRACT**

In the present study was observed the influence of gamma radiation in thermal and mechanical properties of the experimental dental composites based on BISGMA/TEGDMA filled with pre-irradiated MMT nanoparticles (Cloisite<sup>®</sup> 20A). MMT nanoparticle was pre-irradiated at doses of 10, 15 and 70 kGy. As a control group MMT nanoparticle was added in the polymeric matrix without pre-irradiation. Four formulations of experimental nanocomposites were studied all with 50% wt of filler. The characterization of the experimental composites was performed by means of the following techniques: Thermogravimetry Analysis (TGA), Elastic Modulus and Flexural Strength. It was observed that the group filled with pre-irradiated nanoparticles at dose of 70 kGy showed a delay in the decomposition temperature when compared to the control group. For elastic modulus the results showed a proportional increase related to the dose of radiation applied in the MMT nanoparticle. Regarding flexural strength, the groups filled with pre-irradiated nanoparticles and the control group presented similar results.

## **1. INTRODUCTION**

Nanoparticles are widely used as fillers in polymer systems, which are epoxy resins, polyurethanes, polyimides, polyesters, polypropylene, polystyrene, polysiloxanes [1], nitrile rubber, styrene-butadiene rubber, natural rubber, isobutylene and isoprene rubber polymers and polymers of ethylene propylene [2]. Nanoparticles are also very useful on dental materials [3].

In dentistry, over the years, there has been a breakthrough in improving the properties of dental materials due to the addition of nanoparticles. According to previous studies [4], the incorporation of MMT nanoparticles in restorative dental composites has the ability to reduce the residual stress and polymerization shrinkage and improve lifetime performance, abrasion resistance and mechanical properties. The MMT nanoparticles generally have surface treatment performed with the application of quaternary ammonium salts that expands the lamellae [5].

Nanoparticles treated perform important characteristics for the useful life of the composites such as wear resistance, resistance to degradation by the absorption of humidity,

improvement of mechanical strength, physical and chemical properties besides the reduction of costs and weight [6].

The MMT nanoparticles contain many hydroxyl groups that can be modified after gamma irradiation. The stable radicals created during the high-energy radiation exposure are able to initiate bonds between the organic parts responsible for compatibilization with the polymer matrix [7-8]. Due to the high energy transferred by the radiation of gamma source to the nanoparticles of MMT, one of the characteristics observed were the excitation of electrons and ions [9], which can cause reactions in the organic part of the surfactant such as polymerization, crosslinking, grafting and degradation [10].

The purpose of this study was to evaluate thermal and mechanical properties of experimental composites filled with pre-irradiated MMT nanoparticles (Cloisite 20A).

## **2. EXPERIMENTAL**

### **2.1. Materials**

For the formulation of the polymer matrix, the following materials were used: TEGDMA (triethylene glycol dimethacrylate) produced by Esstech (Essington, PA); Bis-GMA: [bisphenyl A bis (2-hydroxy-3-methacryloxypropyl) ether] manufactured by Esstech (Essington, PA); DMAEMA: [2- (dimethylamino) methyl methacrylate, 98%] manufactured by Sigma-Aldrich (Germany); Camforquinone: (camphorquinone, 97%) by Sigma-Aldrich (Germany); MMT Cloisite<sup>®</sup> 20A manufactured by BYK Additives, USA.

According to the manufacturer, MMT nanoparticle (Cloisite<sup>®</sup> 20A) was previously made organophilic through surface modification by hydrogenated quaternary ammonium tallow (2M2HT), in the concentration of 90 meq/100 g<sup>-1</sup> clay, chloride anion, where “Tal-low” represents an alkyl group (with approximately 65% of C18; 30% C16; and 5% C14).

### **2.2. Preparation of Samples**

The experimental nanocomposites were prepared by manual mixing for the homogeneous incorporation of inorganic filler into the polymeric matrix according to reported procedures [4]. After manipulation of the polymer matrix the inorganic filler (MMT Cloisite 20A) was added in small amounts until complete incorporation. The same procedure was made for all groups. To obtain a homogenous mixture each sample was mixed for 5 min.

Formulation of experimental groups is in Table 1.

**Table 1: Formulation of the experimental groups.**

Compound	Group 1 (g)	Group 2 (g)	Group 3 (g)	Group Control (g)
BisGMA (monomer)	0.245	0.245	0.245	0.245
TEGDMA (co-monomer)	0.245	0.245	0.245	0.245
Canphoroquinone (photo-iniciator)	0.005	0.005	0.005	0.005
DMAEMA (amine)	0.005	0.005	0.005	0.005
MMT / 10 kGy (filler)	0.500	-----	-----	-----
MMT / 15 kGy (filler)	-----	0.500	-----	-----
MMT / 70 kGy (filler)	-----	-----	0.500	-----
MMT (filler)	-----	-----	-----	0.500
Total mass	1	1	1	1

Irradiation was carried out on a Multipurpose Radiator with  $^{60}\text{Co}$  source. The doses of radiation used were 10, 15 and 70 kGy and dose rate was of  $5.72 \text{ kGy/h}^{-1}$ . Specimens of 100 mg were prepared for the thermogravimetric test. For elastic modulus and flexural strength tests all the samples were prepared with 10 mm x 2 mm x 1 mm dimension. The samples were photopolymerized ( $n = 10$ ) using the Raddi-cal LED light curing  $1200 \text{ mW / cm}^2$  (SDI Dental Limited, Australia) at wavelength 440 nm - 480 nm.

### 3. METHODOLOGY

#### 3.1. Thermogravimetric Analysis

The decomposition profile and thermal stability of the specimens were observed by thermogravimetric analysis ranging from 25 to 800 °C at the heating rate of  $10 \text{ °C min}^{-1}$  on nitrogen atmosphere on a Mettler Toledo TGA/SDT851(Germany) equipment.

#### 3.2. Elastic modulus and Flexural Strength

For the elastic modulus and flexural strength test, the specimens were subjected to three-point flexing in a universal test machine (Instron 5565 Canton, MA) with a cross speed of 0.5 mm / min and 8 mm a distance between the stand. The three-point method was used 24 hours after the polymerization of the specimens.

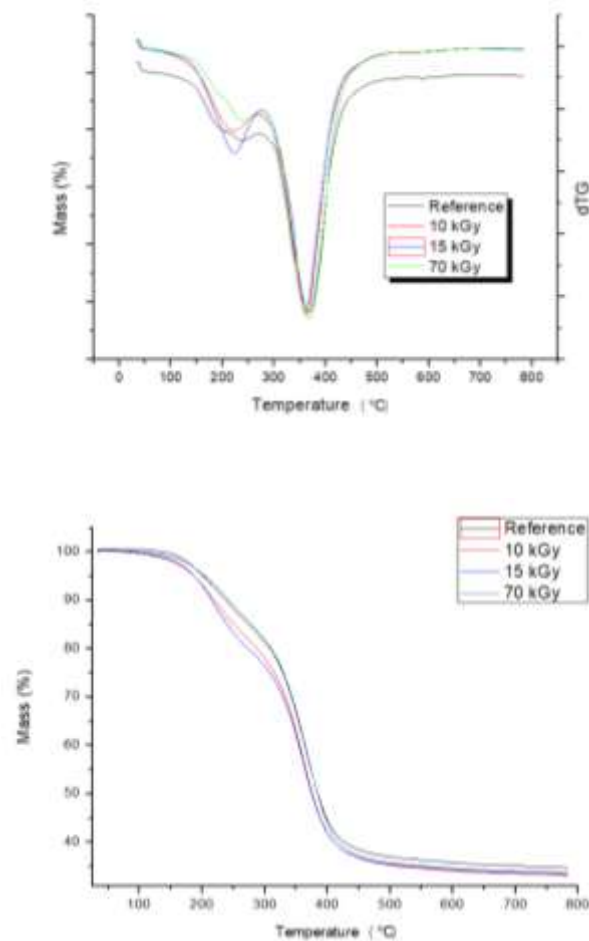
#### 3.3. Fourier Transform Infrared Spectroscopy (FTIR)

The analyses were performed by Fourier Transform Infrared Spectroscopy (FTIR) using KBr pellets. The objective was to identify and evaluate the absorption bands related to the inorganic clayey load. The equipment used was ThermoNicolet 6700 - FTIR Spectrometer with scanning ranging from  $4000 \text{ cm}^{-1}$  to  $500 \text{ cm}^{-1}$ , in IPEN's Lab.Pol./CQMA.

## 4. RESULTS

### 4.1. Thermogravimetric Analysis (TGA)

The results of the thermal stability analysis showed a decomposition profile of the specimens when subjected to a heating program under nitrogen atmosphere. The mass loss was observed by the gradual increase of temperature (25 to 800 °C). The most significant mass losses of the control group occurred between 140 and 240 °C, with a 10% loss in the first mass loss event and between 300 and 370 °C with a 26% loss in the second event. For the experimental composite group irradiated with 10kGy this loss (10%) started between 110 and 220°C (first event) and 24% between 280 and 360°C (second event). For the group irradiated with 15 kGy this loss (10%) started between 125 and 220°C (first event) and 24% between 275 and 360°C (second event). In addition, in the group irradiated with 70kGy, the initial mass loss was of 10% and occurred between 130 and 240°C. At the second moment, between 275 and 370°C, the loss was 21%, a characteristic behavior of mass loss of said polymeric matrix [11], as fig. 1.



**Figure 1: TGA and dTG curves of experimental composites incorporated with MMT (irradiated and non-irradiated)**

The polymer matrix was composed approximately with 49% (wt) of BisGMA (Bisphenol A glycidyl methacrylate), 49% (wt) of TEGDMA (triethylene glycol dimethacrylate), 1 % (wt) of Canphoroquinone (photo-initiator) and 1 % (wt) of DMAEMA (amine). BisGMA has an extensive molecular chain length and an aromatic structure at the center of the molecule. These characteristics are responsible for the two most significant loss events [11]. The results of the TGA analyses showed two events of significant mass loss for all the groups, as also observed in the literature [8]. The first event of mass loss occurred at lower temperatures (140-260 °C) and is due to the scission of the primary chains of the polymer matrix. The second event (260 - 440 °C) occurs due to the decomposition of the main chain evidencing the complex matrix architecture [11].

Comparing the thermal degradation curves of the groups of experimental composites, it is observed that the radiation interferes in the decomposition of the material. The thermal decomposition profile of the experimental composites is directly related to the chemical affinity of the inorganic filler in relation to the polymer matrix. A higher chemical affinity was observed in the group of experimental composite filled with 70 kGy pre-irradiated clay nanoparticles, which was not observed with the low-dose irradiated material (10 and 15 kGy). According to the previous studies [8], MMT nanoparticles contain many hydroxyl groups that might be modified upon gamma irradiation.

#### 4.2. Elastic Modulus (EM) and Flexural Strength (FS)

It was observed that the pre-irradiation interfered in the EM values. There was a gradual increase, according to the doses applied when compared to the control group. For FS, there was no significant difference for the groups when compared to the control group.

**Table 1: Elastic Modulus (EM) and Flexural Strength (FS) values.**

Groups (50% of filler)	Flexural modulus (GPa)	Flexural Strength (MPa)
Control	1.18 (0.72)	27.48 (7.5)
10kGy	1.35 (0.85)	26.96 (5.8)
15kGy	1.49 (0.85)	27.16 (10)
70kGy	1.59 (0.71)	28.25 (9.4)

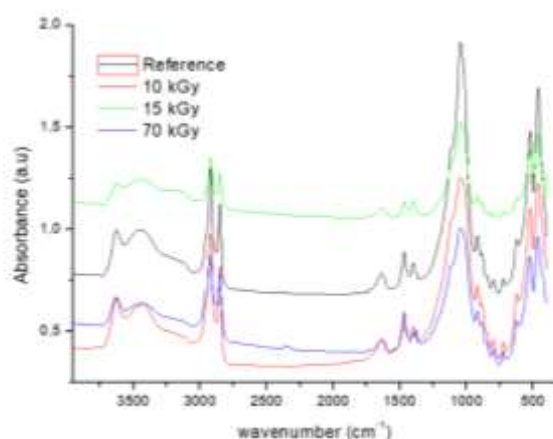
Elastic Modulus may be related to the high rigidity and high modulus that the constituents of the laminated silicate nanoparticles of MMT possess [12].

The results obtained in this study suggest that the radiation does not change the values of the Elastic Modulus since all the groups have a homogeneous composition.

Previous studies report that there was no significant difference between the groups regarding flexural strength at the 25kGy and 50kGy doses [8]. FS values observed in the present study showed that the pre-irradiated groups did not show improved properties when compared to the control group. MMT particles agglomeration is the weak point and the main reason for reducing the strength of a material, even if this agglomeration is strong enough to increase the initial modulus [12].

### 4.3. Fourier Transform Infrared Spectroscopy (FTIR)

The peak observed at the wavelength of  $3630\text{cm}^{-1}$  is related to the binding of the O-H hydroxyl groups originated from MMT. The peaks at  $2843$  and  $2920\text{cm}^{-1}$  correspond to the symmetrical and asymmetric stretching of the C-H groups. The peak at  $1031\text{cm}^{-1}$  is characteristic of the C-H-Si bond. An earlier study showed that for the 25 and 50kGy doses, peak absorption at the  $1717\text{cm}^{-1}$  wavelength was absent for the control group. It is justified by the degradative oxidation with the formation of carbonyl groups in the organic portion of the clay that was explained by the higher chemical affinity between this organic portion and the polar part of the polymer matrix [8]. This peak was not observed in any of the groups analyzed in this investigation (Fig. 2).



**Figure 2: FTIR Spectra of pre-irradiated nanoparticles clays.**

## 5. CONCLUSIONS

By means of the TGA analyzes, it was concluded that the pre-irradiation of the MMT nanoparticles did not interfere in the thermal decomposition of the experimental composites, except the group filled with the nanoparticle irradiated in the dose of 70 kGy, where it was observed a delay in the temperature of decomposition. In the FTIR analysis, no changes were observed in the bands related to the formation of carbonyl groups, as observed in previous studies. Regarding the mechanical properties, the groups filled with pre-irradiated nanoparticle presented higher Elastic Modulus values, compared to the control group. However, this improvement was not observed in Flexural Strength.

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## REFERENCES

1. V. Favier, G.R. Canova, S.C. Shrivastava, J.Y. Cavaille, “Mechanical percolation in cellulose whiskers nanocomposites”, *Polym. Eng. Sci.* Vol. **37**, pp. 1732-1739 (1997).
2. D.J. Harris, T.J. Bonagamba, K. Schmidt-Rohr, “Conformation of poly (ethylene oxide) intercalated in clay and MoS<sub>2</sub> studied by two-dimensional double-quantum NMR”, *Macromolecules*, Vol. **3**, pp. 6718-6724 (1999).
3. Campos, L.M.P., Lugão, A.B., Vasconcelos, M.R. e Parra, D.F., “Polymerization Shrinkage Evaluation on Nanoscale-Layered Silicates: Bis-GMA/TEGMA Nanocomposites, in Photo-Activated Polymeric Matrices”, *Journal of Applied Polymer Science*, pp. 131-2830 (2014).
4. Campos, L.M.P., Boaro, L.C., Santos, L.K.G., Parra, D.F. e Lugão, A.B., “Influence of ionizing radiation on the mechanical properties of BisGMA/TEGDMA based experimental resin”, *Radiation Physics and Chemistry*, Vol. **35**, pp 115-30 (2015).
5. Lertwimolnun, W. e Vergnes, B., “Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix”, *Polymer journal*, Vol.**46**, pp. 3462–3471 (2005).
6. Nowicki, A., Przybytniak, G., Kornacka, E., Mirkowski, K. e Zimek, Z., “Radiation-induced modification of montmorillonite used as filler in PP composite”, *Radiation Physics and Chemistry*, Vol. **76**, pp. 893-900 (2007).
7. Ray, S. e Okamoto. J. “Polymer/layered silicate nanocomposite:A review from: preparation to processing”, *Journal of Applied Polymer Science*, Vol. **8**, pp. 1539-1604 (2003).
8. Campos, L.M.P., Zaharescu, T., Boaro, L.C., Santos, L.K.G., Santos, T.M.R., Ferreira, H.P. e Parra, D.F. “Thermal and mechanical behavior evaluation of dental composites filled with irradiated montmorillonite”, *J. Appl. Polym. Sci.*, Vol. **45063**, pp. 1-6. (2017),
9. De Paoli, M.A “Degradação e Estabilização de Polímeros, Formas Independentes de iniciação das Reações de Degradação”, 2º ed. *Artliber*, São Paulo, Brasil (2008),
10. Jipa, M. I., Stroescu, M., Stoica-Guzun, A., Dobre, T., Jinga, S. e Zaharescu, T., “Effect of gamma irradiation on biopolymer composite films of poly (vinyl alcohol) and bacterial cellulose”, *Nuclear Instruments and Methods in Physics*, Vol. **278**, pp. 82-87 (2012),
11. Sideridou, I.D. e Karabela, M.M., “Sorption of water, ethanol or ethanol/water solutions by light-cured dental dimethacrylate resins”, *Dent. Mater*, Vol. **27**, pp. 1003 (2011).
12. Hussain, F., Chen, J. e Hojjati, M., “Epoxy-silicate nanocomposites: cure monitoring and characterization”, *Mater Sci Eng.*, 467–476 (2007).