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Influence of Alumina Nanoparticles on the Mechanical Properties of a Bioresin Composite

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Abstract: *The aim of this study is to characterize (wettability, surface roughness and gloss) and test (microhardness and diametral compression) four types of light-cured composite resins, one of which is commercial. The first lab-made composite is the reference, obtained by mechanical mixing of three monomers, in equal concentrations. The following two lab-made materials can be considered nanocomposites because they were mechanically mixed in the base solution (Bis-GMA/TEGDMA/Bis-EMA) with α-Al_2O_3 nanopowders, with a concentration of 5 wt.% for one solution and 10 wt.% for the other. The benchmark material comparison for these lab-made composite and nanocomposite resins is the bioresin system, Filtek™ Supreme Ultra Universal Restorative. Results were promising, especially for the 10 wt.% Al_2O_3/Bis-GMA/TEGDMA/Bis-EMA system, characterized by mechanical improvment in comparison with the reference composite.*

Keywords: *bis-GMA/TEGDMA/Bis-EMA resin composite, Al_2O_3 nanoparticles, mechanical testing*

1. Introduction

Composite biomaterials are gaining rapid appreciation in research and industry due to the exceptional versatility of various properties, especially for the nanocomposite types [1]. The synergic effect between the resin, or resin system, and nanomaterial means that all intrinsic properties of the nanofiller will be donated to the matrix, which in return will lead to an increase in overall properties of the material [2].

For a better understanding of resin-based dental composites, numerous evaluation methods are employed [3]. Among material characterizations, the mechanical properties are considered of great importance. Modulus and strengths of dental composites are factors in their development, which are dependent on composition, sample preparation and geometry.

These properties are determined through flexural, biaxial flexural, compressive and diametral tensile tests [4-7]. Another mechanical property is the surface hardness, which in many cases, the Vicker's hardness method is often used [8, 9]. This method is also a good instrument in observing possible crack initiations.

Although there are a high number of mechanical tests for dental materials, it is not clearly understood material mechanism of resistance/failure. Most researchers postulate exclusively that the chemical structure is responsible for the mechanical behaviour of the material [10, 11]. Currently, these explanations are only presumptive because there is no appropriate monitoring system at a molecular level, where the alterations between chains and groups of polymers are spontaneous and almost impossible to observe.

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Among the most used resins in dental materials are the epoxy systems [12], bisphenol A-glycidyl methacrylate (Bis-GMA) [13], urethane-dimethacrylate (UDMA) [14], triethylene glycol dimethacrylate (TEGDMA) [15]. These resins are well known for their lower price, compared to porcelains, and reliable potential in making medical-related products especially on account of the suitable properties of resistance to abrasion, moderate polishing requirements and manageable shrinkage [16-18].

Parallel to the resin systems, progress was the discovery of composite resins [19] such as Vertise Flow (Kerr Corporation), Beautifil II (Shofu Inc.), Filtek™ Supreme Ultra Universal Restorative (3M Oral Care), etc. These composite/nanocomposites have micro- or nano- fillers incorporated in the dental resin matrix with the role of better restorative properties [18]. Aluminium oxide (Al_2O_3) is recognized as an inert material [20], excellent resistance to corrosion and wear and good mechanical results [21].

For this study, the authors chose to opt for the use of two aluminium oxide nanoparticle concentrations, 5 wt.% and 10 wt.% and observe their influence on Bis-GMA/TEGDMA/bis-EMA properties. From our knowledge, the influence of Al_2O_3 nanoparticles on the mechanical properties of the considered resin system has not been discussed.

2. Materials and methods

2.1. Materials

Bis-GMA (bisphenol A glycerolate dimethacrylate, $C_{29}H_{36}O_8$, MW: 512.6 g·mol^{-1}) was used as base monomer resin. BisEMA (ethoxylated bisphenol-A dimethacrylate, $C_{39}H_{44}O_8$, MW: 468 g·mol^{-1}) and TEGDMA (triethylene glycol dimethacrylate, $C_{14}H_{22}O_6$, MW: 286.2 g·mol^{-1}) were utilized as co-monomers. Camphorquinone (CQ) (0.2 wt.%) was used as a photosensitizer. Ethyl 2,4-dimethyl-benzoate was intended as an amine. The stated materials were acquired from Sigma Aldrich. The aluminium oxide nanoparticles (30 nm, α-Al_2O_3) were purchased in nanopowder form from MSE Supplies. For a commercial dental biocomposite, used as a comparison of this research materials, Filtek™ Supreme Ultra Universal Restorative (3M, USA) [22] was used.

2.2. Manufacturing of biomaterials

The substances were mechanically mixed for 24 h in a light-enclosed container, according to the recipes presented in Table 1.

Table 1. Material compositions and other details for the studies of this work

Material code	Resin compositions	Filler type	Filler conc. [wt.%]
M0	*G-T-E:* 50:25:25*	-	-
M1	*G-T-E:* 50:25:25*	α-Al_2O_3, 30 nm	5
M2	*G-T-E:* 50:25:25*	α-Al_2O_3, 30 nm	10
Filtek™ Supreme Ultra Universal Restorative	Bis-GMA/UDMA/ TEGDMA/BisEMA**	Non-aggregated 20 nm SiO_2/ 4-11 nm ZrO_2, aggregated 20 nm SiO_2 and 4 to 11 nm ZrO_2**	72.5**

G-T-E:* Bis-GMA, TEGDMA, BisEMA system, * Information offered by the manufacturer*

After complete homogenization and assuring that there are no gas bubbles in the solutions, light-curing procedures were conducted with a LED (light-emitting diode) poly wave transmission curing device (Bluephase Style, Ivoclar) in single exposure for 60 s at their centre, the same for all solutions. As a rule, for all analysis types, 5 samples were made for each batch, and depending on test-type different moulds. After manufacture, samples were cleaned under ultrasound and stored afterwards in distilled water for 48 h. The use of Bis-GMA:TEGDMA:BisEMA=50:25:25 ratio was influenced by the work of Goncalves et al (2009) [15].

After the materials synthesis is finalized, all materials were subjected to polishing respecting the procedures of Rodrigues-Junior et al (2015) [23]. The multistep polishing system of choice, based on their research, was Sof-Lex Pop on (3M, USA), which consists in 3 grit types (Dark orange, Light orange and Yellow) from medium to superfine. The procedure was made manually with dental equipment, for a more accurate simulation of real clinical conditions.

2.3. Experimental procedures

After the polishing procedure, the finished surfaces of the samples were analyzed for 2D roughness (R_a) with a Surftest SJ-210 profilometer (Mitutoyo, Japan). Values were reported as the average from 15 readings.

Wettability measurements of the samples were conducted by the contact angle method with a goniometer (Kruss DSA30, Germany). The contact angle is understood as the angle between a drop of water (pure water) and the surface of the tested sample. A total of 20 readings were made for each dropping.

Surface gloss was measured using a Novo-Curve glossmeter (Rhopoint Instrumentation, UK), with a square area of 4 mm^2 and 60° testing angle. The device was calibrated according to the manual, after every test on a reflective standard. The measurement unit was gloss units.

For the hardness experiment (ISO6507-1), the materials were tested using a Duramin Model 05656242 (Struers, Denmark) with a Vickers diamond indenter head tip. Based on the indentation parameters, the microhardness was calculated as follows:

$$VH=1.8544 \cdot F/d^2 \quad (1)$$

where: VH = microhardness [MPa]; F = loading mass [kg]; d = average diagonal distance of the indenter mark [µm]. The load of choice was 500 g and the indent time was 15 s.

The samples for surface roughness, wettability, surface gloss and microhardness tests were in disk-form, with 10 mm in diameter and 2 mm thickness.

Diametral tensile strength has been used for the investigation of the nanocomposite resins fracture resistance, using an Instron Universal testing machine, with a cross-head speed of 5 $mm \cdot min^{-1}$. The composite solutions were set into cylindrical moulds (internal diameter: 6 mm; height: 3 mm) according to the method of Penn et al (1987) [24], followed afterwards by light cure and storage, as discussed. The equation for Diametral tensile strength (D.T.S.) is as follows:

$$D.T.S.=2P/(\pi \cdot \phi \cdot h) \quad (2)$$

where: P = loading value at fracture [N]; ϕ and h are the initial diameter [mm] and height [mm] of the tested samples.

3. Results and discussions

3.1. Roughness

The term polishing refers to a surface roughness reduction and scratch-removal occurred by previous finishing process [25]. The importance of good polishing is to prevent bacterial adhesion on the tooth or restoration, which was proven to appear because the high surface roughness [26]. To be more precise, according to literature, a roughness threshold of 0.2 µm or smaller has been suggested as decreasing bacterial accumulation [1, 27, 28].

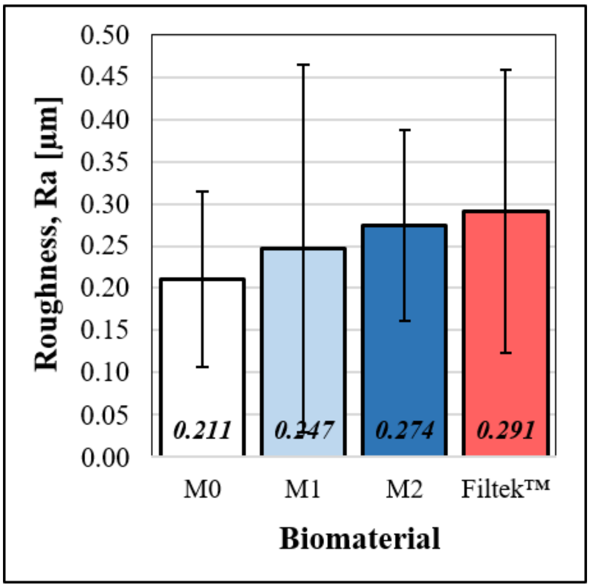

Figure 1. The surface roughness of the studied composites

In the observations offered in Figure 1, the reference sample (M0, without nanoparticles) had the lowest roughness values. This observation could be rational since the polish result is uniform over the entire surface of the sample. In the case of modified resin systems (M1 and M2), due to higher nanoparticle concentration, greater roughness values were produced, comparable to those of commercial nanocomposite resins. Here, due to the presence of hard nanomaterials, it is possible that the polishing procedure was not as efficient as for the reference material.

3.2. Gloss

Gloss is an optical phenomenon understood as the amount of light reflected by the surface of a material at an approximately equal angle at surface irradiation.

Gloss experiments have a relatively easy principle of operation, but the results are very valuable. It plays a very important role in dental restoration's esthetics due to gloss differences between restoration and surrounding enamel, which are easily detected by the human eye [29].

Gloss is in general influenced by material microstructure, average dimensions, form and refraction index of the composite filler, followed by the viscosity, homogeneity and index of refraction of the filler-matrix system [29, 30]. Lefever et al (2012) [29] stated that the gloss of a filler-matrix system will decrease with increase in filler size and also with lowering homogeneity characteristic.

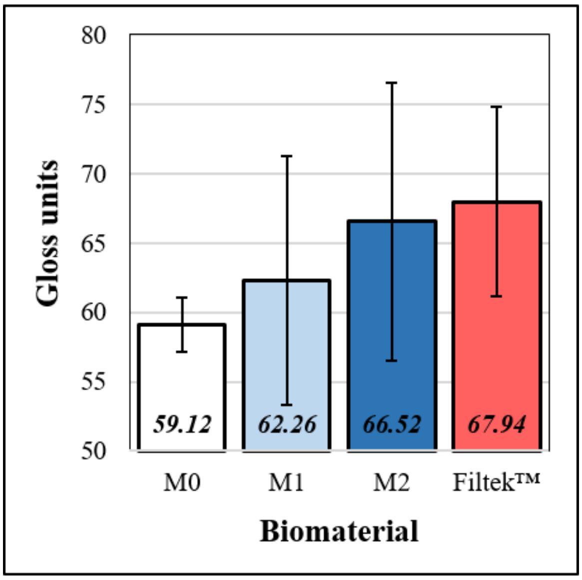

Figure 2. Surface gloss for the studied composite materials

In Figure 2 surface gloss results for the studied materials are presented. It is observed that the increase in nanoparticle concentration, including the commercial resin composite also, led to an increase in gloss characteristics. These results can be explained by the reflective properties of the nanofillers, in which the light rays are reflected better on the nanocomposite surface than the lower or no blended nano-material.

3.3. Contact angle

The contact angle measurements at solid/air/liquid interface is a very utilized technique in investigating the wettability characteristic of solid materials [31]. The mean values of the contact angle and their standard deviations for the studied composites are shown in Figure 3. All results were significantly different between materials. When analyzing the lab-manufactured composites (reference resin and Al_2O_3-blended resins), a linear decrease in contact angle is observed, meaning an increase in the wettability character of the materials. The lowest contact angle is obtained by the commercial resin composite. The highest concentration of nanofillers led to the lowest contact angle. These results are strictly related to the hydrophilic nature of the nanofiller [32]. So, it is logical that an increase in nanoparticle concentration in the resin matrix will lead to a decrease in contact angle, hence an increase in material wettability. According to Gan et al (2012) [33] and Fu et al (2014) [34], commercial dental composites with good wettability should have contact angles in the 31.5° to 64.5° interval. A higher surface wettability will inevitably lead to high water sorption that contributes to the appearance of stains, plaque accumulation and hydrolytic degradation [35].

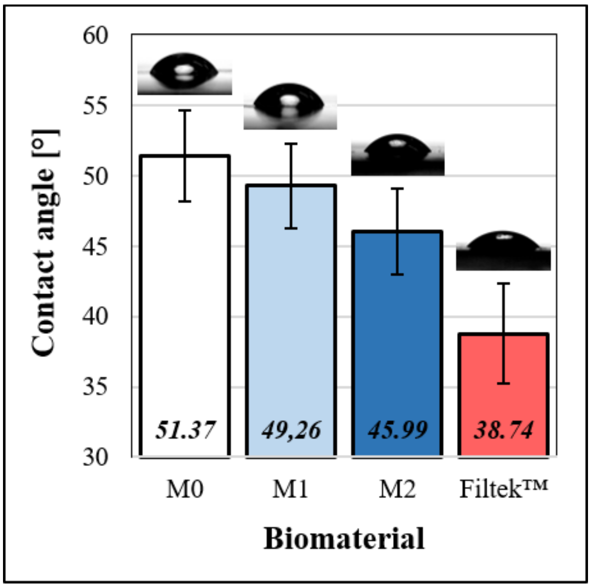

Figure 3. Surface wettability properties of the composites measured with the contact angle method

Based on these optimal contact angle values, the composites manufactured in this study are within the accepted range. On the other hand, better dental material needs to have low wettability properties. Therefore, within the material comparison in this section, the selection of the higher contact angle materials is preferable.

Nevertheless, surface quality is the main factor that influences the diffusion rate of water into the bulk of the material, which controls the degradation and wear resistance.

3.4. Microhardness

Hardness is a key mechanical property for restorative materials, considered in general to be closely

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related to material wear [36]. It is very important that hardness should be similar to the natural materials surrounding it, such as the enamel and dentin tissues, to assure an adequate stress-transfer equilibrium during loading [8]. The hardness of the restorative materials can be modified by the variations of the salivary *p*H.

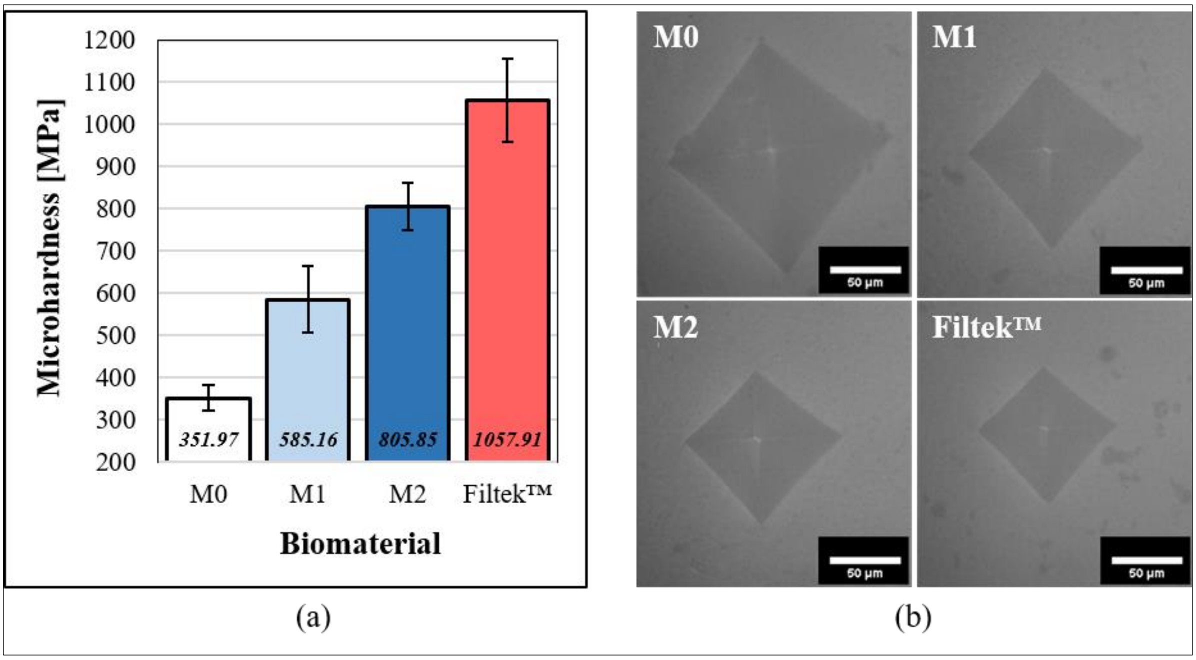

Figure 4. Microhardness of the studied composite materials

In Figure 4(a), microvicker's hardness values are reported for the studied resin composites. The material with the highest hardness, the commercial composite, show a 3-fold increase compared with the reference material. Also, the nanocomposite with 10 wt.% Al_2O_3 presented an increase of approximately 129%, compared with the reference material. The presence of nanofillers led to a hardness increase.

It has been attested that great influence on the mechanical properties of dental resin composites is attributed to the filler content, their size and homogeneity in the resin matrix [36, 37]. Here, it can be remarked that the hardnesses of M2 and Filtek^{TM} composites show the highest values, meaning that filler type, size and concentration offers a positive influence over mechanical properties.

The indentation marks of the tested materials are shown in Figure 4(b). It can be visually seen that the commercial resin composite achieved the least indent and the highest indent imprint was observed for the material with no nanofillers, the reference composite. On a separate remark, it is observed that the polishing procedure was efficient for all materials, which is good evidence for the roughness analysis. Also, no indentation cracks were observed.

3.5. Diametral tensile strength

Determining, through different testing methods, the mechanical properties of dental restorative materials is essential from an engineering point of view [8]. If in the case of hardness, the values of synthetic materials must be relatively similar to the natural ones, in the case of other mechanical properties, such as diametral tensile strength, values should be maximized.

In the case of nanocomposite resins, mechanical stresses are better controlled due to the strong polymer chain-nanomaterial bond. The values of diametral tensile strengths are shown in Figure 5. Diametral tensile strength increases with the addition of nanoparticles into the composite resin.

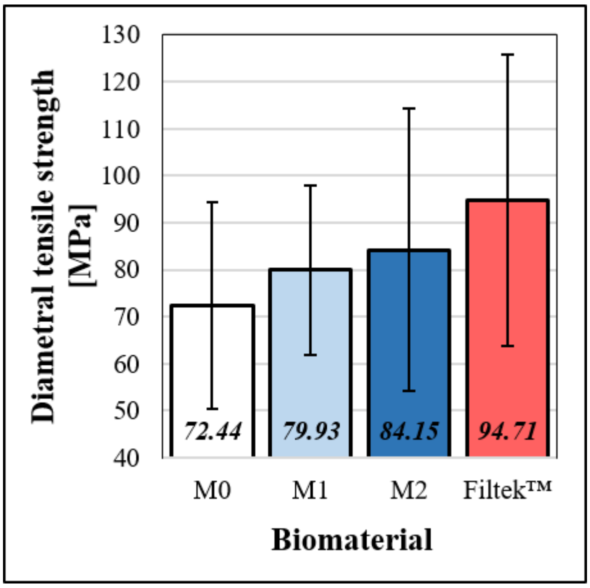

Figure 5. Diametral tensile strength of the studied composite materials

The possible reason for which the diametral tensile strength is higher for M2 and Filtek^{TM} materials is that the high presence of nanoparticles plays a double role, of efficiently controlling stresses caused by pressing (on the imaginary Y-axis of load direction) and also to better control the increasing distance (on the imaginary X-axis of load direction) between the polymer chains, which could otherwise lead to the moment when defects appear, that will inevitably cause the material to collapse. A higher number of nanoparticles will produce stronger polymer chains, leading to delays in the appearance of microcracks, confirming that materials with a high filler content have more favourable mechanical properties.

4. Conclusions

Apart from the concentration of nanoparticles (for lab-made composites), all components and all working parameters were identical to minimize any discrepancy and to facilitate the comparison between materials. The surface qualities of the present restoration materials influence their performance in clinical applications and will affect aspects as form, gloss and roughness. The low wettability properties of the materials are preferable to limit pathogen adhesions or proliferation and to prevent secondary caries. According to these results, the materials with higher contact angles are more beneficial than lower contact angle materials, meaning that, from this point of view, minimizing nanoparticle concentration is a better option. However, when analyzing the other properties, the choice of one of these low wettability materials is not definitive. Under the present conditions, for the mechanical tests, increasing nanoparticle concentration is the best contributor to increasing mechanical properties of the composite materials. Although the commercial composite revealed better mechanical response due to the more complex nanofiller system in the resin composite, the experimental 10 wt.% Al_2O_3 blended nanocomposite could be a competent option especially due to the similar properties, but also in terms of costs, the latter material being composed of a much smaller concentration but also a slightly larger nanoparticle size. Nevertheless, within the limitations of this study, the experimental nanocomposite resins could possess potential in developing onward to clinical testings.

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