

*Dedicated to the memory of  
Professor Petru Spacu (1906–1995)*

## POLYMERIC COMPOSITES FOR DENTISTRY. I

### SYNTHESIS AND CHARACTERIZATION OF A NOVEL DENTAL COMPOSITE WITH POLYMERIC MATRIX

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Novel composite materials based on polymer matrix with inorganic filler have been synthesized and characterized in order to evaluate their potential application in dentistry, as restorative materials. The first approach was to generate and characterize a new filler having the composition in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. The study continued with the development of the polymer matrix based on 2,2 propyl bis-phenyl glycidyl dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) monomers. Composites containing Bis-GMA and TEGDMA at the ratio (wt/wt) of 75/25, filled with different amounts of filler (up to 80% wt) have been prepared. The photopolymerization was induced in the presence of camphoroquinone / N,N-dimethylaminoethyl methacrylate (CQ/DMAEMA), as photoinitiator system. The degree of conversion of each composite was measured by infrared spectroscopy immediately after being cured and it was correlated with the gel content. Water uptake and Vickers' microhardness were evaluated and correlated with the composition of the composites.

## INTRODUCTION

The use of polymer composite materials in dentistry was supported by their properties, namely adequate stiffness, strength and wear resistance, a clinically accepted value of shrinkage and their compatibility with modern diagnostic methods.<sup>1</sup> Dental composite materials based on acrylic resins are an important group of materials in modern dentistry,<sup>2</sup> representing a type of direct aesthetic restorative materials.<sup>3</sup> They have a poly-phase microstructure,<sup>4</sup> being formed by a hydrophobic polymer matrix in which glass, glass-ceramic or ceramic fillers are embedded and it polymerizes upon light exposure.<sup>5</sup>

Despite all the benefits of dental materials available today and studies documenting the longevity of dental restorations made of various materials,<sup>6,7</sup> improvements can still be made. While the filler in the early dental materials was a ceramic oxide like silica or alumina,<sup>8</sup> recent generations of materials have been formulated, containing a high fraction of hard strong particles to produce composites of high strength, approaching that of the tooth structure.<sup>9</sup>

The purpose of the present study was to synthesize and characterize novel composite dental materials, employing a newly synthesized glass in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, with the inorganic phase content in the range of 40, 60, 80% (wt).

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The monomers used were 2,2 propyl bis-phenyl glycidyl dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA). Advantages of using Bis-GMA over the first used small sized dental monomers, or recently developed ring-opening, liquid crystalline, branched and dendritic monomers, include less shrinkage, rapid hardening by free-radical photopolymerization,<sup>10,11</sup> higher modulus and reduced toxicity due to its lower volatility and diffusivity into tissues.<sup>12,13</sup>

## MATERIALS

The patent literature<sup>14,15</sup> disclosed that changes in the dental composite properties resulted mainly from variation in the inorganic filler composition. This study involved a new filler that was reported and characterized elsewhere,<sup>16</sup> which composition is listed in Table 1. The ratio Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> was maintained 1:2 (mole), considered the most appropriate for dental applications.<sup>17</sup>

Table 1

The composition of the glass filler (% mole)

Oxide	Composition, % mole	Role in the glass
SiO <sub>2</sub>	50	Base oxide, network former
Al <sub>2</sub> O <sub>3</sub>	25	Improvement of mechanical properties (high wear resistance and fracture toughness)
CaO	20	Anti-plaque effect
CaF <sub>2</sub>	4	Fluoride release Anti-cavity effect
ZnO	1	Anti-bacterial activity Radio-opacity

Note: The synthesized glass was ground to a particle size of <10 µm.

The dimethacrylates used were Bis-GMA and TEGDMA, purchased by Aldrich Chem. Co and they were used as received, without further purification. In order to perform the UV-curing process, camphoroquinone (CQ) and N,N-dimethylaminoethyl methacrylate (DMAEMA) (Aldrich Chem. Co) used as photoinitiators, have been added to each mixture. The newly synthesized filler, with a particle size of <10µm, has been subsequently incorporated into the polymeric matrix using load concentrations of 40, 60 and 80% (wt).

The polymer matrix was synthesized by employing a weight ratio of Bis-GMA to TEGDMA 75/25 (wt%), a ratio at which composite resin exhibits an optimal degree of conversion<sup>18,19</sup> and is suitable for the incorporation of the appropriate amounts of inorganic filler.<sup>20</sup> The weight ratio of CQ to DMAEMA was maintained at 3/1 (wt%).<sup>21</sup>

The two monomers were mixed in a glass container and a highly viscous solution resulted. The CQ, followed by DMAEMA, was added to the homogeneous solution of the monomers and the compounds were mixed together until the photosensitizer was completely dissolved. The incorporation of the inorganic part was manually done in a glass vessel, by gently heating (40°C) and vigorous mixing. The filler was gradually spread and mixed up to visible homogeneous mixtures. Composite pastes were kept in dark (covered with aluminum foil) in the refrigerator and further used.

The curing reaction was performed under nitrogen atmosphere (flux: 20 ml/min) by UV irradiation (Helios Italquartz lamp), at room temperature. The light intensity at the film surface was 50 mW/cm<sup>2</sup>. The UV exposure time varied from 60 to 180 s and was controlled by means of a camera shutter. The syntheses of the composites were performed into special moulds. Each paste (named A-D, as reported in Table 2) was placed into a HDPE mould (25 mm diameter, 1.5 mm thickness). Both top and bottom surfaces were irradiated for 180 s. The rigid disk products were used for further investigations. In the case of some determinations (for the investigation of mechanical properties) the synthesis was performed into bar-shaped HDPE mould (length-50 mm, height-5 mm, width-15 mm) and the irradiation procedure followed the same steps as that involving the disks.

Table 2

The compositions of the experimental materials (% wt)

Material code	Bis-GMA	TEGDMA	CQ	DMAEMA	Glass filler
A	74.02	24.67	0.98	0.32	-
B	44.42	14.80	0.59	0.19	40.00
C	29.61	9.87	0.39	0.13	60.00
D	14.81	4.93	0.19	0.06	80.00

## EXPERIMENTAL

**Kinetics of photopolymerization** was monitored by FTIR analysis (ATI Mattson Genesis Series II Instrument) controlling the disappearance of the methacrylic double bonds located in the range 1630-1650  $\text{cm}^{-1}$ .<sup>22</sup> The double bond conversion was obtained by measuring the change in the area of the absorption band of the methacrylic groups (normalized against aromatic absorption band at 1583  $\text{cm}^{-1}$ ) before and after the UV irradiation. The degree of conversion (DC) was computed with the following formula, for all compositions:

$$\text{DC}(\%) = 100 - \frac{(\text{area aliphatic C=C abs/area aromatic C=C abs})_{\text{after cure}}}{(\text{area aliphatic C=C abs/area aromatic C=C abs})_{\text{before cure}}} \times 100$$

**Gel content** was determined by measuring the decrease in weight after a 24 h dipping at room temperature in chloroform, followed by additional drying.<sup>23</sup> 10 specimen disks were cured as previously described, properly dried in a desiccator containing dried silica gel, weighted and placed in  $\text{CHCl}_3$ . At the end of treatment (24 h), they were removed from the solvent, let to dry for 6 hours in an oven at 60°C and weighted. The drying process was continued for 7 days in air and the samples were weighted again immediately after drying.

**Morphological studies** involved the investigation of the incorporation of the filler into the polymer matrix and it was performed by optical microscopy and SEM investigations. The samples were analyzed using an optical microscope Sony Hi-resolution and a Hitachi S2500 SEM (Hitachi LTD, Mito City, Japan), after having been metallized.

**Water sorption** investigations involved 10 specimen disks, cured as previously described, that were prepared and placed in a desiccator containing dried silica gel. After 24 h they were removed, stored in an oven at 25°C for 1 day and weighted. After this procedure, they were immersed in water at 37°C for 7 days (when the equilibrium was reached), then removed, dried for 2 minutes in air and weighted ( $m_2$ ). After the weighting, the specimens were reconditioned to a constant mass ( $m_3$ ). The values of water sorption (WS) were calculated for each disk using the following formula:<sup>24</sup>

$$\text{WS} = \frac{m_2 - m_3}{V}$$

where  $V$  ( $\text{mm}^3$ ) is the volume of each composite.

**Vickers microhardness** was measured on 10 specimen disks, at ten different randomly selected sites on each specimen and the mean value was calculated. The equipment employed was a Vickers microhardness equipment-Leitz Wetzlar (Germany) that measures the indentations at a microscopic level. Vickers microhardness number (VHN) was determined from the following equation:

$$\text{VHN} = 1.854 \times \frac{P}{d^2}$$

where  $P$  is the load (kgf) and  $d$  the length of the diagonal indentation (mm) (arithmetic mean of 10 measurements).

## RESULTS

Based on literature scrutiny,<sup>25</sup> that revealed that an approach involving an initial low radiant exposure produced a significant reduction in contraction stress compared to a single, continuous exposure, the considered irradiation was of 50  $\text{mW/cm}^2$ . The irradiation was performed in steps of 60s, as it was suggested that the delay time relieves stresses forming during the initial exposure.

Since further reduction in residual monomer level may occur by continuing polymerization of the monomers, the obtained materials were further treated at 60°C<sup>26</sup> and let to postpolymerize.<sup>27</sup> Fig. 1 presents the change in absorbance for the D composition as a function of the irradiation time. The comparison of conversion depending on the glass content is presented in Fig. 2 and the conclusion was that the DC increases with the glass content.

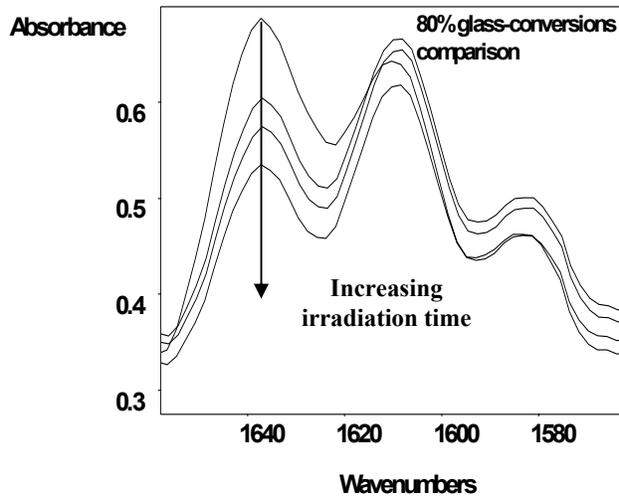


Fig. 1 – FTIR absorbance for 80% load composite (code: D), before and after 60s, 120s and 180s irradiation (cumulative).

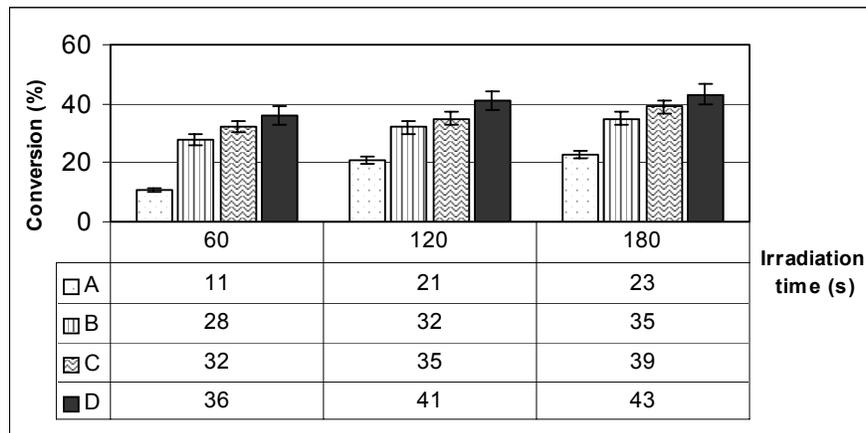


Fig. 2 – The dependency conversion (%) – composition - irradiation time for the composites. The bar within the box represents the standard deviation of the data set.

Concerning the gel content, it has been estimated that the maximal release of unreacted monomers from Bis-GMA/TEGDMA composites occurs within the first 24 h.<sup>28</sup> The corresponding data are presented in Fig. 3 and they are in good agreement with other studies involving diacrylate networks.<sup>29</sup>

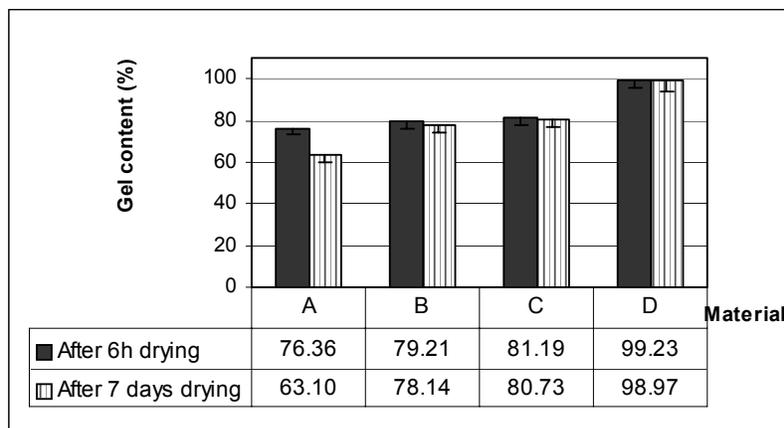


Fig. 3 – Gel content of the composites. The bar within the box represents the standard deviation of the data set.

The morphological studies revealed that the distribution of the glass inside the polymer matrix is quite homogeneous (see Fig. 4). Fig. 5 shows two SEM micrographs (using different enlargements) of the 80% loaded composite revealing the sizes below 10 $\mu$ m (Fig. 5 (a)) and the inclusion of a glass particle into the polymer matrix (Fig. 5 (b)).

Fig. 4 – Microscopic structure of the surface of the 80% load composite.

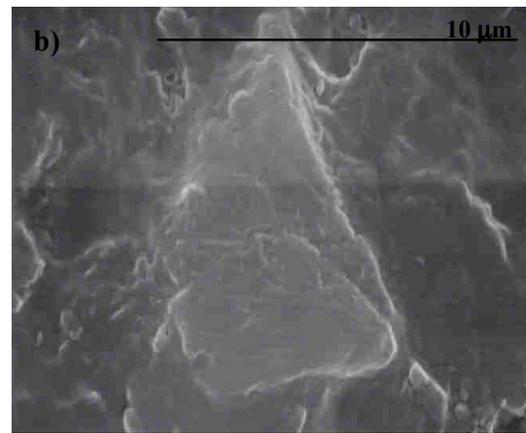
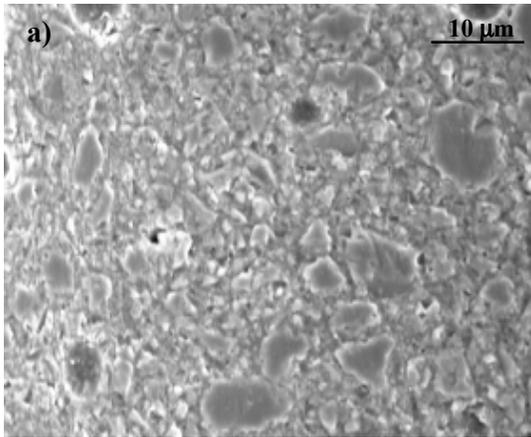
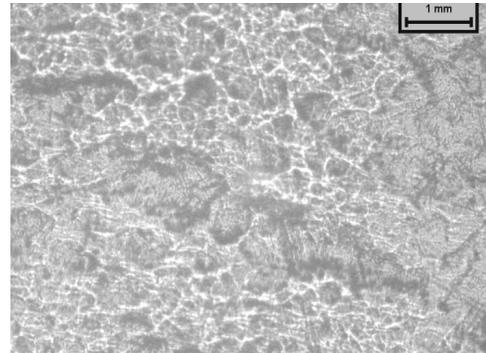


Fig. 5 – SEM micrographs of the 80% load polished composite emphasizing a) particle sizes and b) the glass inclusion into the matrix.

According to ISO 9000s standard for dental restorative resins, water sorption should be less than 50  $\mu$ g/mm<sup>3</sup>.<sup>30</sup> The values of water sorption (reported in Fig. 6) for all the materials investigated are within the range of the ISO's standard, the best composites being those containing 80% glass particles (code D).

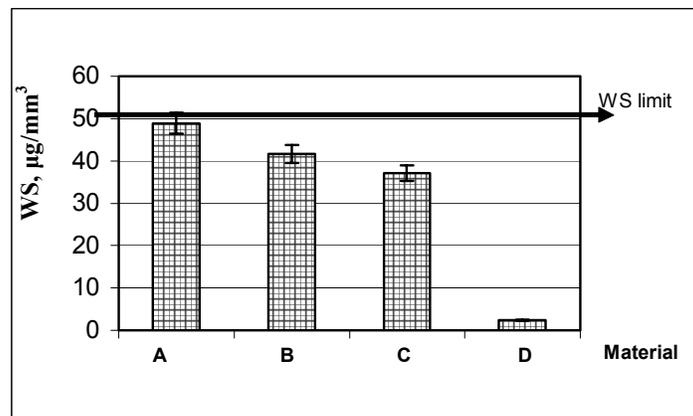


Fig. 6 – Water sorption ( $\mu$ g/mm<sup>3</sup>) function of the glass content. The bar within the box represents the standard deviation of the data set.

In order to study the effect of the filler content on the mechanical properties of the composites, the microhardness was investigated employing Vickers method.<sup>31</sup> As expected, the increasing of the microhardness with the filler content was noticed (Fig. 7).

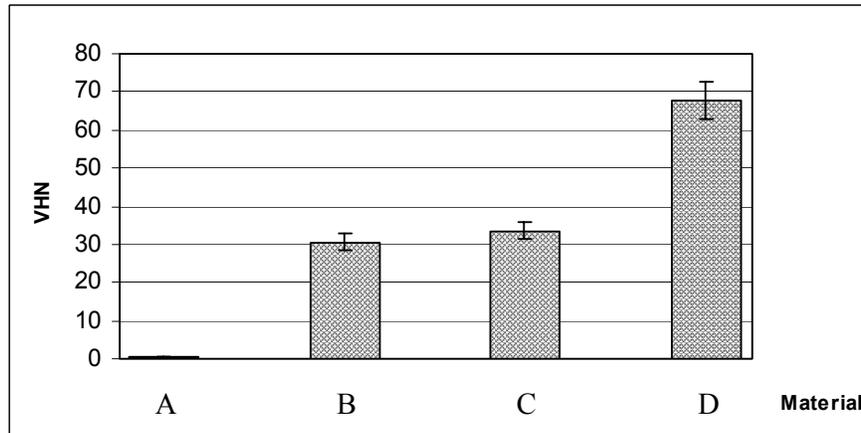


Fig. 7 – Microhardness dependency on the glass content.  
The bar within the box represents the standard deviation of the data set.

The mechanical properties of the resin composites improved with irradiation time. This is mainly due to an increase in the photopolymerization efficiency, as revealed by other studies, as well.<sup>29</sup> Fig. 8 shows VHN results obtained by testing samples with known degrees of monomer conversion measured by FTIR.

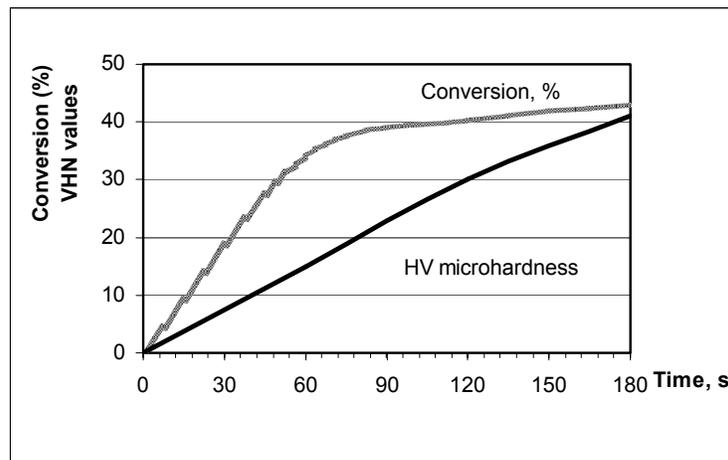


Fig. 8 – Microhardness evolution during photopolymerization of the 80% load composite.

## DISCUSSION

Dispersion of a large fraction of filler into the highly viscous resin matrix represents a rather difficult technical problem, as there is the possibility of an insufficient amount of resin to completely fill the interstitial space. We have chosen 10 $\mu$ m particle size in order to combine the advantages of macro and microfine fillers, in a random distribution, being know the fact that microfine materials commonly exhibit aggregation. The decrease of the particle size might be done, but at the expense of filler loading, while the general interest is to obtain higher filler incorporation, as increased filler content improves mechanical properties and reduces the curing shrinkage.<sup>32</sup> In addition, the final composite materials will be subjected to a temperature range from 0°C up to 60°C (usually taken as extremes met in the mouth) when a composite containing microfine filler showed poorer properties than

that containing loading of coarser filler.<sup>33</sup> In this work irregularly shaped particles have been employed because of their better mechanical retention in the resin.<sup>34</sup>

The photopolymerization of multifunctional monomers is a complex process as regards their kinetics.<sup>35,36</sup> The dimethacrylate system undergoes extensive cross-linking on polymerization, with considerable residual unsaturations in the final product. However, in terms of biocompatibility, the unreacted monomer seems not to offer serious or irreversible biological environmental damage.<sup>37,38</sup>

As regards conversions, we assumed that the activating light efficiency increases due to multiple light scattering by filler particles, at high filler loading, this phenomenon being reported also by other studies.<sup>39</sup> Another aspect is the effect of the cure time that caused a significant DC increase. It is clear that employing longer irradiation time, a conversion higher than 43% may be obtained (however in the range 55-70%<sup>40</sup>). The known limiting degree of conversion of the Bis-GMA alone is 40%, while that of the pure TEGDMA is 70%.<sup>41,42</sup>

The conversions obtained by FTIR do not agree with those resulted from the gel content. The first method (FTIR) refers only to unreacted double bonds (as a whole), while the second (gel content) is based on the extraction of whole monomer units (each compulsorily containing both unreacted double bonds).<sup>43</sup> However, extraction and determination of unreacted free monomers using gel content is a convenient method to measure the residual amount of whole monomer units and we consider that it gives useful information. The unconverted methacrylate groups might reside in the polymer network either as residual monomer (being trapped inside the network) or as pendant side chains that extend from the main chains by virtue of having reacted at only one end of the difunctional molecule.

The sorption of water in glassy polymers is generally described by a dual-mode theory, which assumes that the amount of the sorped molecules consists of two populations. One is held by ordinary molecular dissolution in the polymer matrix according to the Henry's law and the second is trapped in polymer microvoids following the Langmuir isotherm.<sup>44,45</sup> As polydimethacrylates are crosslinked glassy polymers, the presence of crosslinks between polymer chains generally results in a significant decrease in the solvent permeability of polymer because they decrease the hole free volume and the ability of polymer chains for swelling.<sup>46</sup> However, on one hand, the sorption of water may be considered a desirable effect as the hygroscopic expansion of composites has been demonstrated to close marginal leakage gaps due to shrinkage.<sup>47</sup> On the other hand, an important criterion for dental composites is adequate resistance to degradation by water and other solvents. Dental composites were reported to leach only 0.25-0.95% of their total mass into aqueous solution within the first 30 days, this being attributable mostly to the inorganic part.<sup>32</sup>

There is a clear direct correlation between microhardness and DC, as a consequence of the increase in stiffness and strength of the composites due to the polymerization process.

## CONCLUSIONS

The present study focused on the synthesis of a new Bis-GMA-based composite resin with innovative filler to be used in dentistry as a restorative material. The newly synthesized filler was a white powder, with particle sizes carefully selected.

The degree of conversion of each composite was measured by FTIR immediately after being cured and was correlated to the gel content experiments. Other physical properties were also investigated, namely water sorption and Vickers microhardness. The present investigation have established the following facts, some of them confirming already reported data: (1) DC increased with filler content due to light scattering, (2) cure time caused a significant DC increase, the last method being a good indicator of the postpolymerization process; (3) there is a direct correlation between the DC and Vickers microhardness, (4) most of the unconverted methacrylate groups seemed to be in the form of pendant side chains, extended from the main chains, (5) water sorption values for all studied materials were within the range of the ISO's standard.

The composite materials, developed with a filler content of 80%wt showed better properties compared with other synthesized materials, proving to be potentially useful in dental composites area.

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