

THE STUDY OF NEW COMPOSITES WITH GRAPHENE USED IN DENTISTRY

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ABSTRACT. The development of graphene nanopowder in a polymer matrix has opened, in recent years, a new and exciting area in the science of dental materials. Physico-chemical and mechanical properties of these materials are improved at a very low filler loading in the polymer matrix. The novelty of this study is the utilization of graphene-silver nanopowder as filler in new dental composites to improve the physico-mechanical properties. Three experimental composites, two with different percent in graphene-silver nanopowder and one commercial nanohybrid composite Herculite XRV Ultra (Kerr) were investigated by water absorption and solubility in distilled water and artificial saliva (1, 7, 14 and 21 days), respectively flexural strength and Young's modulus properties. One-way analysis of variance (ANOVA) test, for multiple comparisons between means to determine significant differences was used at a significance level set at $p \leq 0.05$. The experimental results show that composite with a greater amount of graphene (G2) present better results of water absorption and flexural strength.

Keywords: *graphene, dental composites, water sorption, flexural strength*

INTRODUCTION

The development of graphene nanopowder in a polymer matrix has opened, in recent years, a new and exciting area in the science of dental materials. These nanohybrid materials show a significant improvement in physico-chemical and mechanical properties that cannot normally be achieved using conventional composites, especially for dental composites. The extent of the improvement is related directly to the degree of nanofillers dispersion

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in the polymer matrix. The most important aspect of composites with graphene-silver nanopowder is that all these improvements are obtained at very low filler loading in the polymer matrix [1-4]. There have been studied most graphene composites according to the type of the processing method, the polymer matrix and fillers, but none is being used in dentistry. The interaction mechanism in (polymer/graphene/nanofiller of glasses) composites used in dentistry depends on: polarity, molecular weight, hydrophobicity, particles size and shape, reactive groups, etc., present in the polymer, graphene and nanofiller [5-7]. Composites used in dentistry are available as hybrid types, containing milled glass fillers and discrete nanoparticles (40–50 nm) and as nanofill types [8,9]. They containing both nano-sized filler particles, called nanomers, and agglomerations of these particles described as “nanoclusters”. Polymer composites absorb water and release unreacted monomers in an aqueous oral environment. The water ingress into dental composites in the oral cavity can, over time, lead to deterioration of the physical/mechanical properties. There are studies on water absorption [10-13] or ethanol/water solution [11] or ethanol [12] for experimental and commercial light-cured dental composites.

The novelty of this study is the utilization of graphene-silver nanopowder as filler in new dental composites to improve the physico-mechanical properties.

In this study we have three experimental composites, two with different percent of graphene-silver nanopowder, comparing with commercial nanohybrid composite Herculite XRV Ultra (Kerr), in determination of water absorption and solubility in distilled water and artificial saliva (1, 7, 14 and 21 days), respectively flexural strength and Young's modulus properties. The values reported in tables and figures represent mean values and standard deviation of replicates. One-way analysis of variance (ANOVA) test, for multiple comparisons between means to determine significant differences was used at a significance level set at $p \leq 0.05$.

RESULTS AND DISCUSSION

Studies determining the water sorption and solubility of composite materials used in dentistry are especially important for their relative values, while numerical comparisons are not always possible.

The preparation, characterization and properties of graphene as filler in different composites for a large number of polymers are discussed in most papers [14,15,16]. Most of the properties of polymer/graphene composites were superior to the base polymer matrix as well as other carbon filler (carbon nanotubes, carbon nanofiber, and graphite) based composites. These improved properties of the composites are obtained at very low graphene contents (≤ 2 wt%).

Water sorption is different in many studies [17] and there are several factors influencing water uptake values. Water sorption is a diffusion-controlled process that occurs in the organic matrices, but the kinetics of water sorption is slower for some resins and may not have reached equilibrium even after several days [18]. In these study composites with greater amount of graphene presented low solubility in saliva and higher solubility in water. The composite experimental without graphene is maintained at constant value in both water and saliva, in solubility and absorption.

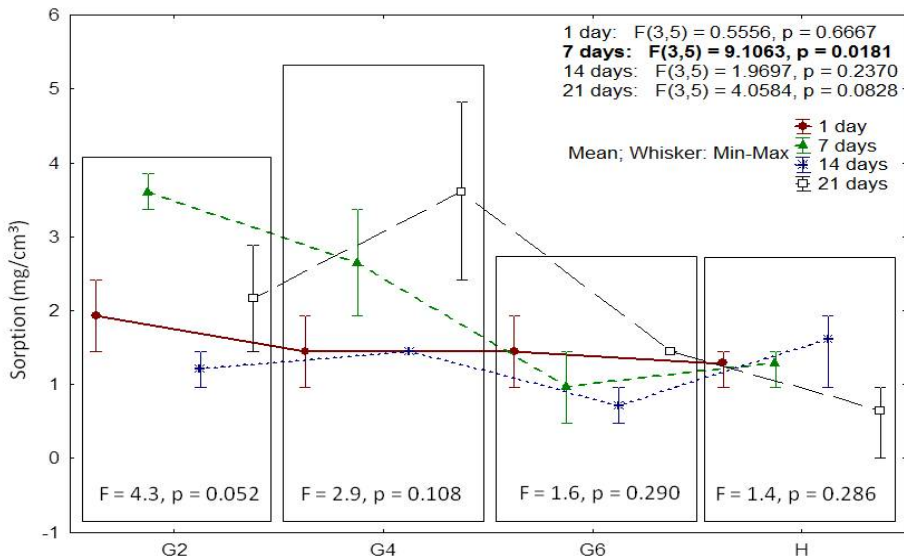


Figure 1. The statistical parameters from testing ANOVA at water sorption in distilled water when the comparison has been done for the same day (1, 7, 14, 21) so that it can be seen if is a statistically significant difference between the type the sample for the same day. The statistical parameters obtained through ANOVA test, when comparisons has been done for the same group (G2, G4, G6, H) such that it can be seen that there is no a statistically significant difference between days at same sample type.

Considering only the same day (Figure 1) as a factor, we can say that the studied composite materials G2, G4, G6 and H have a different evolution of water absorption over time, depending on the immersion solution used in the study (Figure 1, 2). In the case of samples immersed in water statistically significant differences were found between measurements made on 7 and 21 days, not identifying significant pairs. For samples in artificial saliva significant differences could not be identified (Figure 2). Water absorption material was identified as having significant values in the case of samples immersion in

water. Immersion in artificial saliva does not seem to determine significant differences in absorption between materials. Comparing the studied composites can be seen (Figure 1) that G2 and G4 had statistically significant differences compared to the Herculite, for water immersion. There were no significant pairs on the artificial saliva immersion studies.

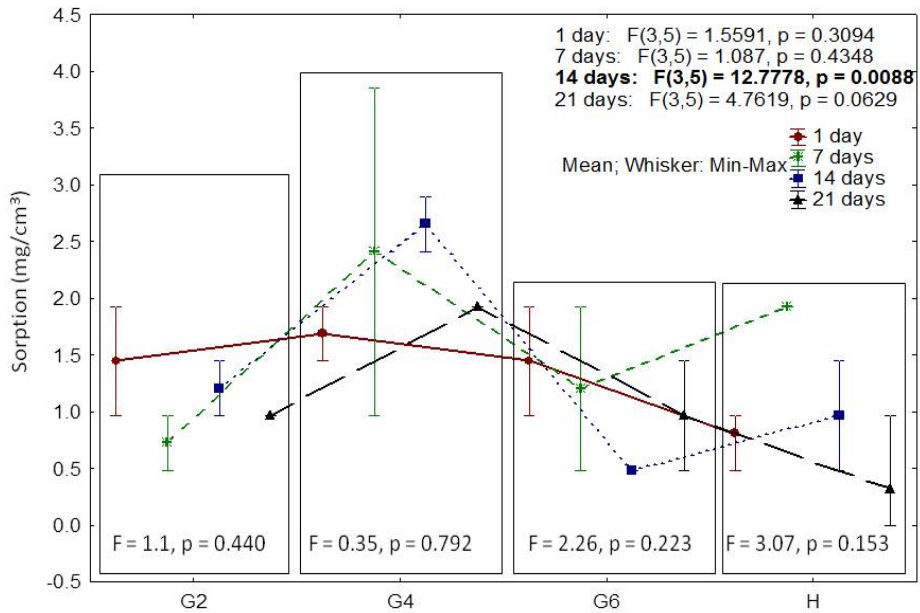


Figure 2. The statistical parameters at water sorption in artificial saliva, when the comparison has been done for the same day (1, 7, 14, 21) so that it can be seen if is a statistically significant difference between the type the sample for the same day. The statistical parameters at water sorption in artificial saliva, when comparisons has been done for the same group (G2, G4, G6, H) such that it can be seen that there is no a statistically significant difference between days at same sample type.

It shows a trend of water absorption increasing for G4 material; a final value at the end of the study relatively equal with the beginning value of the study for the G2 and G6 experimental materials and a slight decline for Herculite. Even if the differences of absorption values can be seen during the experiment, the final value is close to the initial measured value.

Taking into account only the time as a factor, we can say that the studied materials have different solubility evolution (figure 3, 4) in time, regardless of the immersion solution used in the study. A pair wise comparisons material has highlighted that G4 material presented statistically significant differences compared to other materials in both immersion solutions.

THE STUDY OF NEW COMPOSITES WITH GRAPHENE USED IN DENTISTRY

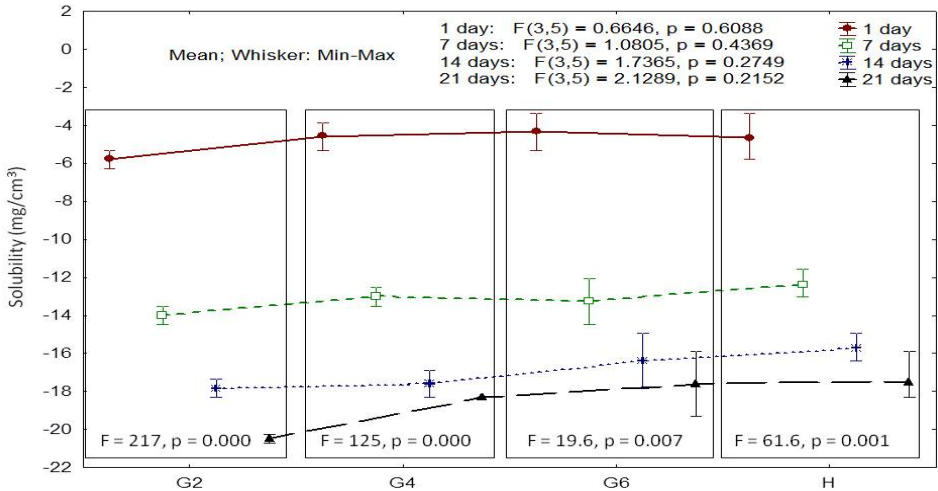


Figure 3. The statistical parameters from testing ANOVA at solubility in distilled water when the comparison has been done for the same day (1, 7, 14, 21) so that it can be seen if is a statistically significant difference between the type the sample for the same day. The statistical parameters obtained through ANOVA test, when comparisons has been done for the same group (G2, G4, G6, H) such that it can be seen that there is no a statistically significant difference between days at same sample type.

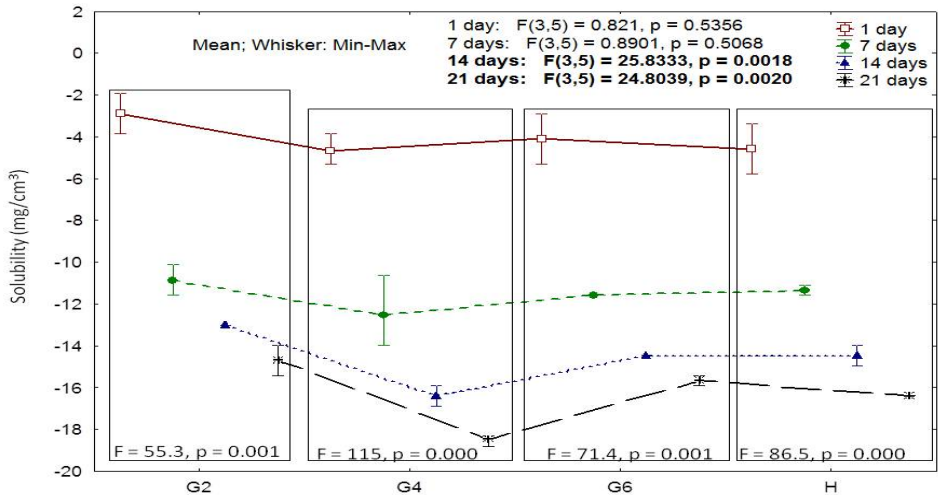


Figure 4. The statistical parameters from testing ANOVA at solubility in artificial saliva, when the comparison has been done for the same day (1, 7, 14, 21) so that it can be seen if is a statistically significant difference between the type the sample for the same day. The statistical parameters obtained through ANOVA test, when comparisons has been done for the same group (G2, G4, G6, H) such that it can be seen that there is no a statistically significant difference between days at same sample type.

Evolution water solubility (figure 3) of the four materials studied it is considered significantly different only between G2 and G4 composites respectively G4 and Herculite. For solubility in artificial saliva (figure 4) it is considered significantly different only between G2 and H composites, respectively G4 and G2. Comparing these two charts remark that the solubility in artificial saliva (figure 4) is lower than solubility in water (figure 3) of experimental materials, while for Herculite composite the values is similar in both medium.

Differences in the chemical composition of the composites considerably influence the degradation behavior of the resins [19]. This is attributed to the different chemistry of their organic matrix. The organic matrix of experimental and commercial composites consists of Bis-GMA and TEGDMA, aromatic and aliphatic dimethacrylate monomers, and show that the aromatic content is higher than that of the aliphatic [20]. Artificial saliva or water uptake in the organic matrix of polymer composites causes generally two opposing processes. The solvent will extract unreacted components, mainly the residual monomer, loss of weight and reduction in mechanical properties [21, 22].

The results obtained for the flexural strength and flexural modulus of the studied composites after immersion in water $37\pm 1^{\circ}\text{C}$ for 24 hours are shown in figure 5.

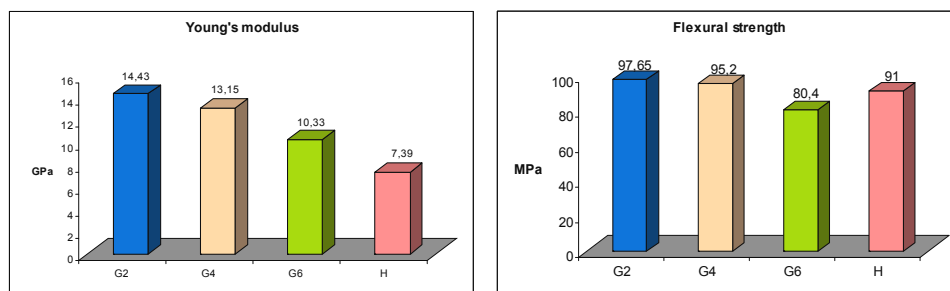


Figure 5. The average values for: a) Young's modulus and b) Flexural strength recorded after 24 hours in distilled water at 37°C for two composite G2 and G4 with the graphene, two composite, without the graphene, G6 and H

After immersion in distilled water for 24 hours at 37°C of the four materials studied (G2, G4, G6 and Herculite), G2 showed the greatest flexural strength, and followed by Herculite. This result shows that the flexural strength depends not only on the filler content but also on the filler chemistry. The composite G2 have in composition 10 wt % nanopowder with graphene (HA-Ag graphene). The flexural modulus of composites after immersion for 24 hours day follows the order $\text{H} < \text{G6} < \text{G4} < \text{G2}$. Comparison of flexural strength after immersion for 24 hours in water showed the values obtained are comparable and no significant difference was observed for the other

composites. Comparison of flexural modulus after immersion in water did not show any significant difference ($p < 0.05$) for 24 hours at 37°C. Several researchers [23] have determined the intrinsic mechanical properties of the single, bi- and multiple layers of graphene. After polymerization the composites were immersed in water and artificial saliva. Water or artificial saliva uptake in the polymeric phase of dental composites causes generally two opposing processes. The solvent will extract unreacted components, mainly the residual monomer which leads to loss of weight and reduction in mechanical properties.

CONCLUSIONS

Correlating the results for sorption in water and artificial saliva with mechanical properties (flexural strength and Young's modulus) we can conclude that the experimental composites with a greater amount of graphene (G2) shows better results. After carbon nanotubes, graphene has been reported to have the highest elastic modulus and strength.

EXPERIMENTAL SECTION

Materials

One commercial and three experimental restorative materials were selected for evaluation from physico-mechanical point of view (Table 1).

Table 1. Description of materials used in this study

<i>Material</i>	<i>Organic Phase</i>	<i>Inorganic phase</i>	<i>Company</i>
<i>Experimental nanocomposite G2</i>	<i>Bis-GMA TEGDMA</i>	<i>HA-Ag graphene 10% (%wt) Sr-Zr glass Quartz</i>	<i>ICCRR Cluj-Napoca</i>
<i>Experimental nanocomposite G4</i>		<i>HA-Ag graphene 5% (%wt) Sr-Zr glass Quartz</i>	<i>ICCRR Cluj-Napoca</i>
<i>Experimental nanocomposite G6</i>		<i>Sr-Zr glass Quartz HA</i>	<i>ICCRR Cluj-Napoca</i>
<i>Herculite XRV (H)</i>	<i>Ultra Bis-GMA TEGDMA</i>	<i>Barium glass filler Colloidal silica Prepolymerized filler</i>	<i>Kerr</i>

Bis-GMA - 2,2-bis(4-(2'-hydroxy-3'methacryloyloxy-propoxy)phenyl)propane; **HA** - hydroxylapatite (synthesized in ICCRR Cluj-Napoca laboratory); **TEGDMA**- triethyleneglycol- dimethacrylate (Aldrich); **DMAEM**-2-dimethyl(aminoethyl)methacrylate (Aldrich); **Cq**- camphorquinone (Aldrich).

The *inorganic filler* consists of silanized powders based on mixture of colloidal silica - SiO₂ (Degussa), hydroxyapatite (HA) with 15% graphene-silver nanoparticles and Sr-Zr bioglass (35-SiO₂, 20-SrO, 10-ZrO₂, 10-Al₂O₃, 13-B₂O₃, 6-NaF, 6-CaF₂, wt.%), obtained as a mass through the conventional melting method in ICCRR laboratory. Surface treatment of the fillers was made by γ -methacriloyloxypropyl-trymethoxysilane (A174) (Aldrich).

Graphene-silver nanoparticles (Gr-Ag) composite were synthesized by the Radio-Frequency catalytic Chemical Vapor Deposition (RF-CCVD) method [12] using silver nanoparticles distributed over magnesium oxide (Ag_x/MgO, where x = 3 wt.%). The synthesis was performed using a methane flow rate of 80 mL/min and a reaction time of 60 minutes [24].

The *HA- graphene-silver* nanoparticles (Gr-Ag) were synthesized by precipitation of HA in presence of graphene-silver. The starting materials were CaO, H₃PO₄ (Aldrich) for synthesis of HAP. The mixed sols were subjected to heat treatment at 120°C and 400°C for 2 h.

The *organic matrix*- monomers mixture consists of: Bis-GMA/TEGDMA in 65/35 ratio. Bis-GMA was synthesised in ICCRR laboratory.

The *experimental composites G2, G4, G6* were prepared as monopaste, by dispersing in the organic matrix the silanized bioactive inorganic fillers, in ratio 20/80 wt.%. The commercial composite Herculite XRV Ultra (**H**), in ratio 21/79 wt.%, was used as a reference material. In order to initiate the photochemical curing, there have been introduced in the monomer mixture an initiator system consisting of: *photosensitizer* - camphorquinone (Aldrich) 0.5% relative to the liquid mixture and a *polymerization accelerator* 2-dimethyl (aminoethyl)methacrylate (Aldrich) 1%.

Methods

A total of four groups were formed. For the water sorption and solubility measurements, ten disc specimens were prepared for each material. A mold for the preparation of a disc specimen 15+1 mm in diameter and 1 mm thickness was used. Sorption and solubility tests were determined according to the method described in ADA Specification No. 27-1993/ISO 4049/2000 regarding filling materials.

The specimens were light-cured, under a glass microscope slide, with an activated light source (Woodpecker®Dental Curing Light LED.B lamp) polymerization unit. The samples were irradiated in different positions for 40 s until the entire area was exposed. The discs removed from the mould were dried in the desiccator in the presence of calcium chloride at 37 ± 1° C for 24 hours. Before being weighed, the specimens are kept in the desiccator at 23° C. Weighed discs are divided into 2 groups, prior to be immersed in

distilled water and artificial saliva respectively, at $37 \pm 1^\circ\text{C}$ and maintained for 1:7:14:21 days (during which their weight was measured daily). After this time, discs were removed from water or artificial saliva with tweezers, wiped with paper, air-dried for 15 seconds and 1 minute after removal samples are weighed. The extent of absorption in water and artificial saliva for each disc was calculated using the formula:

$$W_{sp} = (m_2 - m_3) / V$$

where: m_2 - mass of the sample after immersion in water for 24 h (μg)
 m_3 - mass of the sample kept in desiccator until constant mass (μg)
 V - volume of the sample (mm^3)

Solubility tests were performed on the same composites (G2, G4, G6, H). Solubility tests were completed using the same samples as for absorption test, by maintaining the discs in water and artificial saliva at 37°C and values were recorded at 1, 7, 14 and 21 days. Experimental values for solubility are expressed in $\mu\text{g} / \text{mm}^3$ using the formula:

$$SL = (m_1 - m_3) / V$$

Where: m_1 – constant weight of the sample before water immersion (μg)
 m_3 – constant weight of the sample maintain in the desiccator (μg)
 V – Sample volume (mm^3)

The specimens for the mechanical tests, flexural strength (FS), were performed at 23°C , according to ISO 4049/2000. The samples were prepared using teflon molds with $2 \times 2 \times 25 \text{mm}$ which did not offer resistance to the displacement of the specimen, minimizing the formation of cracks and flaws within the bulk material and surface during their preparation. After $24 \pm 1 \text{ h}$, the specimens were loaded at a crosshead speed of 0.5 mm/min until fracture with a Lloyd Instruments-LR5k Plus mechanical testing machine controlled, using the Nexygen Software on a Windows PC.

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