Effects of Graphene Addition on the Mechanical Properties of Composites for Dental Restoration

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Alternative research techniques are essential in order to prove the efficacy of graphene dental materials and their viability, especially if we associate them with other materials studied so far. It is important to determine the effects of these techniques because they can demonstrate the viability and credibility of the research on its properties. The purpose of this study was to measure and analyze the mechanical properties of several composite materials with/without graphene and commercial composite Herculite, designed for dental composites–restorations. The materials were composed of a visible light-curing monomer mixture (Bis-GMA+TEGDMA) as a matrix and hydroxyapatite with graphene, bioglasses, colloidal silica as a reinforcing filler. Ten specimens of different composites were prepared for each mechanical test: flexural strength, Young's modulus, diametral tensile strength, and compressive strength test (Lloyd Instruments- LR5k Plus). Mean values and standard deviations were calculated and ANOVA and Student Newman Keuls multiple comparison tests were applied ($P< 0.05$). The addition of 5-10 wt% of hydroxyapatite with graphene nanoparticles to the unfilled monomer mixtures led to the increase of both Young's modulus, surface hardness of the material, and the flexural strength. Hydroxyapatite with graphene has been used as reinforcing nanofiller in polymeric materials, having potential applications for restorative composites.

Keywords: graphene, hydroxyapatite, dental composites restoration, mechanical properties

One of the major preoccupations of the researchers and the manufacturers, which activate in the field of dental materials, is the obtaining of composite resins with an improved adhesion to hard dental tissues [1]. In theory this purpose can be achieved both through modifying the inorganic or the organic phase. At the same time a good link between them has to be created. The mechanical properties of restorative materials are a crucial factor in their clinical performance and are strongly related to the composition-filler and organic matrix. Graphene-based composites are two-dimensional building blocks assembled in a layer-by-layer hierarchy [2], which can be crosslinked by various chemicals to establish both intralayer, i.e. graphene layers are bridged on the edges, in the same plane, and interlayer load transfer [2-6], having the unique mechanical and transport properties desired for a wide range of technologies. Structural defects are always present in conventional macroscale solids, and thereby their crucial influence on mechanical properties of these graphene composites is inevitable.

This paper is an addition to the recent advances in the modification of powders with graphene and the fabrication of graphene-based polymer composites. Recently, graphene has attracted both academic and industrial interest because it can produce a dramatic improvement in properties at very low filler content. The modification of powders with graphene and utilization of these materials in the fabrication of composites with polymer matrices for dentistry is the novelty. Here, preparation and mechanical properties of polymer/graphene composites are discussed in general along with detailed examples drawn from the scientific literature, compared with composites without the grafene.

Nanotubes of various types have been investigated for dental applications in a number of interesting directions. Titanium oxide nanotubes have been shown in vitro to accelerate the kinetics of HA formation, mainly in a context of bone-growth applications for dental implant coatings[7]. More recently, modified single-walled carbon nanotubes, have been shown to improve flexural strength of hybrid composite. These nanotubes had silicon dioxide applied to them in conjunction with specialized organosilane bonding agents[8]. Currently, synthetic biomaterials (bioceramics and biopolymers) have been widely applied to the tissue engineering fields [9-11]. Also, mechanical properties have attracted considerable attention because composites used in dentistry must have high values.

The purpose of this study was to measure and analyze the mechanical properties of several composite materials with/without graphene, commercial composite Herculite designed for dental composite restorations.

Experimental part

The inorganic phase consists of silanizated fillers system based on mixture between colloidal silica (SiO_2) (Degussa), hydroxyapatite nano-particles (HA) with 15% graphene and bioglass (35-SiO_2, 20-SrO, 10- ZrO_2 10-Al_2O_3, 13-B_2O_3, 6-NaF, 6-CaF_2, wt.%), obtained as a mass through the conventional melting method in ICCRR laboratory. Surface treatment of the fillers was made by γ-methacriloyl-oxypropyl-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

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Table 1
DESCRIPTION OF MATERIALS USED IN THIS STUDY

Material	Organic Phase	Inorganic phase (% by volume)	Company
Experimental composite CG2	*Bis-GMA 65%* *TEGDMA 35%* *DMAEM*	*HA-Ag graphene 10%* *Sr-Zr glass* *Quartz*	*ICCRR Cluj-Napoca*
Experimental composite CG4		*HA-Ag graphene 5%* *Sr-Zr glass* *Quartz*	*ICCRR Cluj-Napoca*
Experimental composite CG6		*Sr-Zr glass* *Quartz* *HA*	*ICCRR Cluj-Napoca*
Herculite XRV Ultra	*Bis-GMA* *TEGDMA*	*Barium glass filler* *Colloidal silica* *Prepolymerized filler*	*Kerr*

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

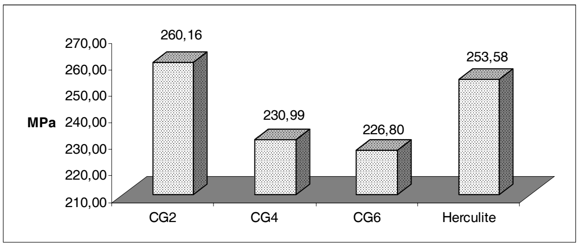

Fig. 1. Compressive Strength

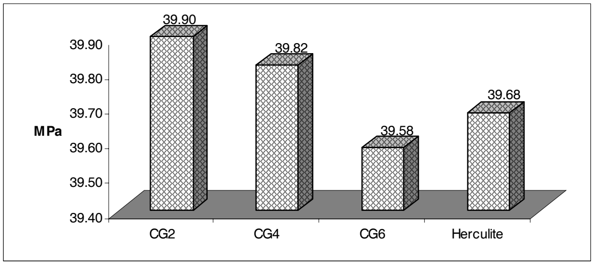

Fig.2. Diametral Tensile Strength

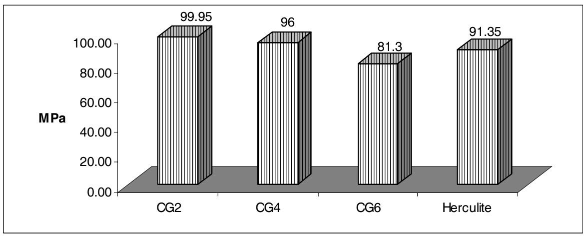

Fig. 3. Flexural Strength

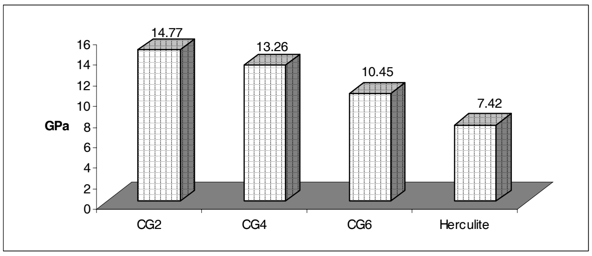

Fig. 4. Young's modulus

methane flow rate of 80 mL/min and a reaction time of 60 min[13].

The *HAP- graphene-silver* nanoparticles (Gr-Ag) are synthesized by precipitation of HAP in presence of graphene-silver. The starting materials were CaO, H_3PO_4 (Aldrich) for synthesis of HAP. The mixed sols were subject to heat treatment at 120 and 400°C for 2 h.

The organic phase - monomers mixture consists of: Bis-GMA/TEGDMA in 65/35 ratio with camphorquinone/amine as initiator/activator system. Bis-GMA was synthesised in ICCRR laboratory, TEGDMA **(**Aldrich**)**, camphorquinone (Aldrich), amine (N,N dimethyl-aminomethyl methacrylate) (Aldrich).

The experimental composites **CG2, CG4, CG6** were prepared as monopaste, by dispersing in the organic phase the silanizated bioactive inorganic fillers, in ratio 20/80 wt.%. The comercial composite Herculite was used as a reference material. In order to initiate the photochemical curing composites 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%.

The specimens for the mechanical tests such as compressive strength (CS), diametral tensile strength (DTS) and flexural strength (FS) were performed at 23°C, according to ISO 4049/2000 and international norms "American Dental Association's Specification" No.27. The samples were prepared using Teflon molds which did not offer resistance to the displacement of the specimen, minimizing the formation of cracks and flaws within the material bulk and surface during their preparation. Ten specimens were prepared for each mechanical test group with different dimensions according to the standard test (6x3mm for DTS; 3x6mm for CS and 2x2x25mm for FS). The composite resins were polymerized with the aid of a Woodpecker® Dental Curing Light LED.B lamp for 60 s, from several directions. After 24 ± 1 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.

Results and discutions

The mechanical properties of the composites without graphene CG6, comercial composite Herculite and CG2, CG4 composites with grafene were investigated by mechanical analyser (Loydd) at 23°C. Mechanical properties of these composites are summarized in figure 1, 2, 3, and 4, which are in good agreement with their ISO description.

For the experimental and commercial composites investigated in this study, the highest values of flexural strength were obtained for CG2 (96.95MPa), followed by composite CG4 (96 MPa), Herculite and CG6 composite. The highest values of the flexural strength (fig. 3) were obtained for composite materials CG2, which has the highest percent in Ag-graphene.

For compressive strength (MPa), ANOVA test results reveal that between the average values of the four composites there are statistically significant differences ($p<0.0001$). The highest value of compressive strength of experimental composite had GC2 (260.16 MPa), and was statistically significant ($p<0.05$) higher than that of composite without graphene CG6 (236.80 MPa). The mean highest to diameteral tensile strength was obtained for the composite CG2 (39.90 Mpa), being higher than the value for composite CG4 (39.82 MPa) and CG6 (39. 58MPa). No significant differences ($p>0.05$) were obtained between the values of the three experimental materials.

The strong chemical interaction between organic and inorganic phase and homogeneous dispersion of grapfene/ hydroxyapatite result in a uniform stress distribution and is able to minimize the occurrence of stress concentration, leading to a significant increase in mechanical properties of the resulting composites. The uniform dispersion, together with the strong interfacial adhesion between graphene/hydroxyapatite, glasses and organic matrix, also enhances the mechanical properties of composites with graphene comparing with Herculite. Although the loading amount of graphene in all composites was not very high, it significantly improves the mechanical properties. Graphene is specifed by extremely high in-plane stiffnes - Young modulus - and superior strength. The exceptional mechanical properties of graphene are of utmost importance for its aplications, because they are highly needed to exploit graphene composite as a superstrong structural material. Young's modulus can be considered a measure of the stiffness of a graphene composite. It is widely used for isotropic and continuous media, in which, the elastic parameters together define the mechanical properties of the material.

The addition of 5-10 wt% of hydroxyapatite with graphene nanoparticles to the unfilled monomer mixtures led to the increase of both Young's modulus, surface hardness of the material, and the flexural strength. In general, when microscopic instead of nanoscopic hydroxyapatite was used as a reinforcing filler, mechanical properties were favoured.

An adequate surface modification of the hydroxyapatite particles conferred enhanced mechanical properties to the final dental composite. Hydroxyapatite with graphene has been used as reinforcing nanofiller in polymeric materials, having potential applications for restorative composites. The filler content, size, type and distribution, as well as coupling between particles and matrix, are factors that influence mechanical properties such as strength and modulus of elasticity.

The experimental composites with/without graphene used in this study showed mechanical properties at least as good as those of commercial composites.

From the study by Ibrahim M. Hamoudi and Hagag Abd Elkader [14], flexural strength values for commercial composite and hybrid nanofillers are between 93.68-89.85 MPa. Letícia C. Boaro and colaborators [15] have studied a variety of different commercial composites and hybrid nanofillers, which gave values between 96-180.9 MPa. Higher results of flexural strength for these materials are probably due to the high content of inorganic phase in combination with an organic phase consisting of monomers with stiffer branches, which are also capable of strong intermolecular interactions. Composites containing different filler particle types and morphologies were used. However individual composite materials responded differently.

Conclusions

The experimental composites with/without graphene used in this study showed mechanical properties at least as good as those of commercial composites.

This study proves that the hydroxyapatite-graphene silver powders provide distinct reinforcing mechanisms, compared with the nanohybrid composites, resulting in significant improvement of the composite strength and reliability. Hydroxyapatite with graphene silver has been used as reinforcing nanofiller in polymeric materials having potential applications for restorative composites.

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