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Flexural strength and elastic modulus evaluation of structures made by conventional PMMA and PMMA reinforced with graphene

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Abstract. – OBJECTIVE: The aim of this study was to compare both the elastic modulus (EM) and the flexural strength (FS) of two materials used in dental prosthesis, namely polymethylmethacrylate (PMMA) and polymethylmethacrylate reinforced with graphene (G-PMMA).

MATERIALS AND METHODS: Twenty rectangular samples were manufactured by a milling machine and divided into two groups (n=10/group): Group 1, PMMA; Group 2, G-PMMA. The specimens were subjected to a three-point bending test conducted in the elastic range to evaluate EM. A similar test was protracted until fracture to evaluate FS. Data on EM and FS were statistically analyzed with independent-samples t-test in order to compare the two groups. A scanning electron microscope (SEM) (5.00 kx and 1.00 kx magnification) was used to evaluate the morphology of sample's fracture.

RESULTS: Compared to PMMA samples, each G-PMMA sample showed significantly higher values of FS (p <0.001) and EM (p <0.001). SEM images analysis showed an inhomogeneous fracture morphology in G-PMMA samples.

CONCLUSIONS: The results show that G-PMMA is a promising material to be used for prosthetic purposes. This is demonstrated by a significant increase in both peak load and bending stiffness, resulting from the bending test performed on G-PMMA samples. Furthermore, the latter exhibit greater homogeneity in their mechanical behavior, supporting the potential value of this material in dental prosthesis.

Key Words:
PMMA, Graphene, Mechanical resistance, Flexural strength, Elastic modulus.

Introduction

Nanotechnology is a field of research concerned with the development of new materials, such as graphene, characterized by different behaviour from their bulk matter counterparts[1]. Novoselov et al[2] have first isolated this material from graphite flakes. Graphene is a crystalline form of carbon. Its structure, which is that of a honeycomb lattice, results from the sp^2 hybridized carbon orbitals. The latter forms a single monolayer packed into a two-dimensional structure[3]. Placed at 120° from each other, carbon atoms are connected through a three σ-bond and an out-of-plane π-bond.

Graphene is a nanomaterial characterized by excellent properties and feasibility[4]. It has a large specific surface area (2630 $m^2 g^{-1}$), high intrinsic mobility (200 000 $cm^2 v^{-1} s^{-1}$), high Young's modulus (~1 TPa) and thermal conductivity (~5000 $Wm^{-1} K^{-1}$)[5]. It can be employed in many fields of research, including electronics, optoelectronics, bioengineering, medicine and, recently, dentistry.

Graphene and graphene-based materials – as graphene oxide (GO) and reduced graphene oxide (rGO) –display many potential applications in dental fields. Among others, these include:

a) Development of platforms able to release therapeutic molecules to improve implants osseointegration and bone formation[6];
b) Development of nanofiller in cements and adhesives, with antibacterial properties against *S. mutans*[7,8];
c) Fabrication of dental prosthesis in addition to other dental materials.

PMMA is one of the most common denture base material, which was first introduced by Walter Wright in 1937 and described by Peyton FA in 1975[9]. It consists of a stratified polymer characterized by a satisfying aesthetic, chemical stability, lightweight, and acceptable cost. Furthermore, it is resistant to corrosion and water repellent. However, the mechanical properties of this material are questionable[10]. To improve the resistance of

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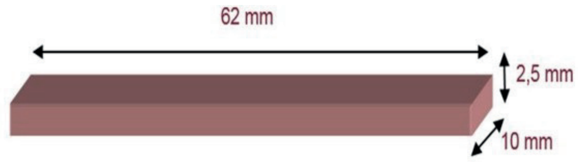

Figure 1. Samples dimensions in accordance with ADA Specification n°12.

denture base resins, different reinforcing agents such as fibers, fillers and rubberlike substances were employed in the past[11].

The aim of this *in vitro* study is to compare flexural strength (FS) and elastic modulus (EM) of both conventional polymethylmethacrylate (PMMA) and polymethylmethacrylate reinforced with graphene (G-PMMA). The results of such comparison enabled us to evaluate the differences in the mechanical properties of both materials.

Materials and Methods

The study was conducted in collaboration with the Department of Astronautical, Electrical, and Energy Engineering of Sapienza University of Rome (Rome, Italy).

Forty samples were used and they were divided into two groups (twenty samples for each group):

1. Conventional PMMA (PMMA);
2. PMMA reinforced with graphene (G-PMMA).

The specimens had a rectangular shape (62 mm length, 10 mm wide and 2.5 mm thick) in accordance with the American Dental Association (ADA) Specification n°12 for denture base polymers[12] (Figure 1).

Specimens were measured using a digital caliper (Aura Dental, Aura an der Saale, Germany) with an accuracy of 0.01 mm. All the samples were fabricated using a Computer-Aided Design/Computer-Aided Manufacturing (CAD/CAM) system with a milling technique. More specifically, G-PMMA specimens were obtained by milling "G-CAM" polymeric discs (98.5 mm in diameter and 22 mm in thickness), produced by Graphenano Dental Company (Valencia, Spain) (Figure 2).

The samples were created by following the phases below:

Scanning of the Wax Model: A red modeling wax was used to create the prototype and it was scanned with a dental lab digital scanner -3shape E3® . The DICOM file was turned into an STL file using the software Cross Manager® (Figure 3A).

Modeling with CAD Software: The STL file was opened and modified in Exocad® software (Figure 3B).

Setting of the Milling Machine: 3D hyperDENT® software was employed to set the milling machine (Figure 3C).

Sample Making: A milling machine – imesicore, CORiTEC 350i® – was used to mill the samples (Figure 3D).

The mechanical test was conducted using a three-point bending test (Instron® testing machine, model 3366).

The main parts of the universal machine include:

- load frame with an integral controller;
- load cell mounted to the crosshead;
- specific fixtures for electromechanical tests;
- Instron® approved computer system with Instron
- Bluehill® software.

During a three-point bending test, a gradual load is applied to the samples by a rounded wedge called "nose". The machine consists of two cylindrical rollers, supporting the sample, placed at the distance of 5 cm (Figure 4).

The FS test was performed using a 10 kN load cell. After a pre-load of about 2 N, the nose started applying the load at 1.0 mm/min crosshead speed and the specimen was deflected until rupture.

A 500 N load cell was used for the evaluation of EM. A deflectometer was mounted underneath the sample and it was connected to an extensometer to register any minimum deformation during the test. The latter was performed with a progressive loading at the 1 mm/min speed and it was stopped when the sample has reached the deformation of 0.5% in order to maintain it in the elastic phase (Figure 5). In both tests data processing was done using the Bluehill 3® software.

Field emission-scanning electron microscope Analysis

All samples were characterized through Field Emission-Scanning Electron Microscope (FE-

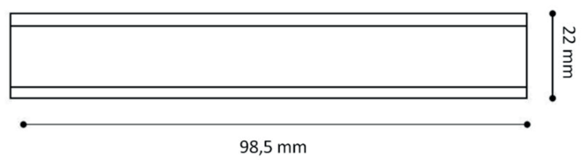

Figure 2. Schematic dimensions of the milling disc.

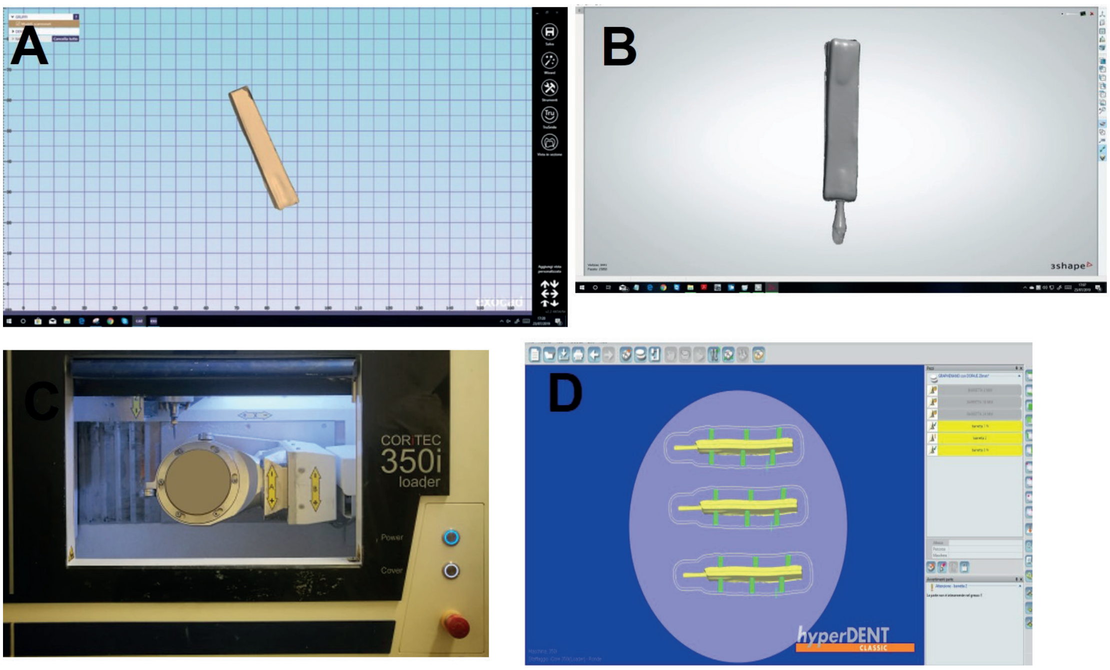

Figure 3. Acquisition and milling of the samples.

SEM) using a Zeiss Auriga FE-SEM, available at Sapienza University of Rome Nanotechnology and Nanoscience Laboratory (Rome, Italy). The FE-SEM images were used to evaluate the fractured surface of both the PMMA and G-PMMA samples. These were examined using an image analysis software (SmartSEM, Zeiss®, Oberkochen, Germany) at 1.00 kx and 5.00 kx magnification.

Statistical Analysis

Data were evaluated using standard statistical analysis software (version 20.0, Statistical Package for the Social Sciences, IBM Corporation, Armonk, NY, USA). A database was created using Excel (Microsoft, Redmond, WA, USA). Descriptive statistics including mean () ± standard deviation (SD) values were calculated for each variable and box plots were used to evaluate data outliers. The Shapiro-Wilk test was used to determine whether the data conformed to a normal distribution or not. The independent-samples *t*-test was carried out to identify statistically significant mean differences in the FS and EM between G-PMMA and conventional PMMA. In each test, the cut-off for statistical significance was $p \leq 0.05$.

Table I. PMMA values of FS and EM. It was calculated the mean and the standard deviation.

Sample	MAX Stress [MPa]	MAX Load [N]	Elastic Modulus [GPa]
1	108.18	165.93	2.91
2	92.53	143.46	2.88
3	94.61	146.27	2.88
4	100.94	154.98	2.88
5	101.77	157.33	2.88
6	90.35	138.45	2.87
7	100.09	153.37	2.88
8	76.57	116.64	2.88
9	95.17	144.97	2.89
10	102.95	158.67	2.88
x	96.32	148.00	2.88
SD	8.78	3.39	0.01

Table II. G-PMMA values of FS and EM.

Sample	MAX Stress [MPa]	MAX Load [N]	Elastic Modulus [GPa]
1	113.03	177.51	2.95
2	113.65	178.48	2.94
3	108.15	171.49	2,92
4	114.03	175.95	2.94
5	110.43	170.90	2.94
6	110.91	171.81	2.98
7	117.85	184.53	2.97
8	113.12	177.32	2.98
9	111.96	174.98	2.96
10	117.12	185.04	3.00
x	113.03	176.80	2.96
SD	2.94	1.12	0.02

Results

Bluehill 3® software created two different stress-strain curves for each material and two tables showing FS and EM values (Figure 6 and Table I for PMMA. Figure 7 and Table II for G-PMMA).

The mean value of FS showed by the G-PMMA before fracture was greater (113.03 ± 2.94 MPa) than the mean value of FS of PMMA (96.32 ± 8.78 MPa).

The addition of graphene to PMMA determined a statistically significant increase of 16.71 ± 2.93 (95% CI, 10.56-22.86) MPa in the FS compared to conventional PMMA (p<0.001) (Table III).

The mean value of EM showed by G-PMMA was greater (2.96 ± *0.02* GPa) than the one showed by PMMA (2.88 ± 0.01 GPa). The addition of graphene to PMMA determined a statistically significant increase of 0.08 ± 0.01 (95% CI, 0.057-0.093) GPa in the EM compared to conventional PMMA (p<0.001) (Table IV).

Both variables analyzed have shown the standard deviation greater in PMMA samples than in G-PMMA samples. This result suggests a more homogeneous mechanical behavior during the bending test of the reinforced PMMA compared to the standard material.

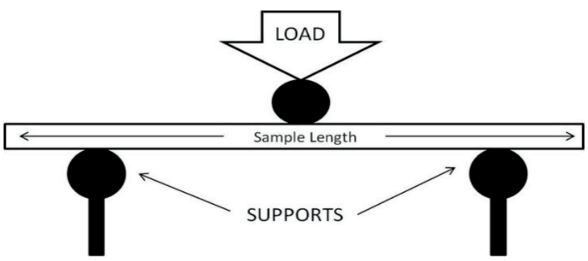

Figure 4. Schematic view of a three-point bending test.

Morphological Characterization of Materials

Different types of fracture resulted from the SEM analysis of the fracture surfaces. PMMA samples showed a flat and morphologically homogeneous fracture, with uniformly distributed irregularities (Figure 8A-8B). G-PMMA samples, on the other hand, showed a morphologically irregular fracture, with several flakes (Figure 9A-9B).

Discussion

According to the Consensus Conference in Chester, UK (1991), a "biomaterial" is a materi-

Figure 5. Detail of a sample in the supports of the Instron machine. Beneath of the sample was fixed the deflectometer connected to the extensometer (in black).

Table III. Difference in the flexural strength between PMMA and PMMA and graphene.

Independent samples test										
	Levene's test for equality of variances		*t*-test for equality of means							
	F	Sig.	t	df	Sig. (2-tailed)	Mean difference	Std. error difference	95% Confidence interval of the difference	
								Lower	Upper
Equal variances assumed	5.508	0.031	5.706	18	0.000	16.70900	2.92832	10.55682	22.86118
Equal variances not assumed			5.706	10.986	0.000	16.70900	2.92832	10.26284	23.15516

Table IV. Difference in the elastic modulus between PMMA and PMMA and graphene.

Independent samples test									
	Levene's test for equality of variances		*t*-test for equality of means						
	F	Sig.	t	df	Sig. (2-tailed)	Mean difference	Std. error difference	95% Confidence interval of the difference	
								Lower	Upper
Equal variances assumed	8.221	0.010	8.915	18	0.000	0.07500	0.00841	0.05733	0.09267
Equal variances not assumed			8.915	12.275	0.000	0.07500	0.00841	0.05672	0.09328

al intended to interface with biological systems to evaluate, treat, improve or replace any tissue, organ or function of the human body. Due to their chemical nature, biomaterials can be distinguished in metals, ceramics, polymers and composites. Specifically, composites derive from the combination of the matrix – generally polymeric – and the charge as reinforcement or filler. The latter improves the mechanical, thermal and electrical characteristics of the polymeric material. The use of graphene as a reinforcement within the nanocomposites is favored by a significant enhancement in its production methods and its low processing costs. Today, few studies in literature have analyzed the characteristics of PMMA-based nanocomposites reinforced with graphene. Alamgir et al[13] investigated the characteristics of a graphene-based PMMA nanocomposite for dental applications. The authors performed a microindentation test to analyze mechanical characteristics and a field emission scanning electron microscopy (FESEM) to determine the morphology of the fracture. The results of the study showed that nanocomposite was more resistant to deformation and had a higher value of Young's modulus than PMMA. Similarly, Khan et al[14] tested a graphene oxide-polymethylmethacrylate composite. Both a three-point flexural test and a wear resistance test were performed to analyze its mechanical characteristics. The results showed a significant improvement of wear resistance and bending test of Graphene Oxide (GO) nanocomposite, compared to the control group (PMMA). In particular, the flexural strength of samples containing GO at a concentration of 0.048 wt/wt.% was 87.0 ± 7.2 MPa compared to 65.9 ± 11.5 MPa of the C-group. Yang et al[15] showed that adding both GO and graphene sheets to PMMA leads to a greater re-

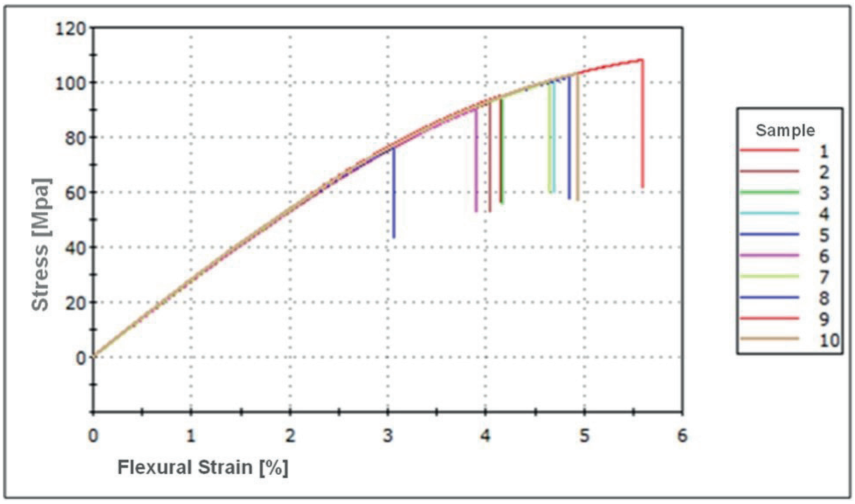

Figure 6. PMMA stress-strain curves.

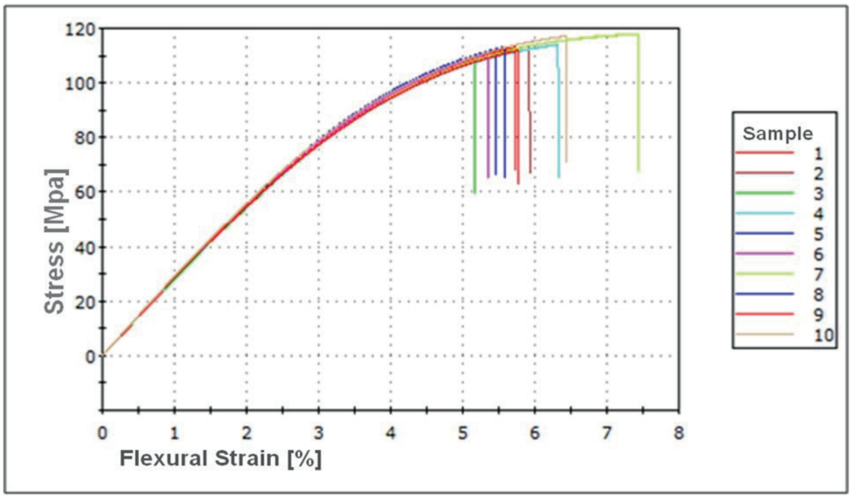

Figure 7. G-PMMA stress-strain curves.

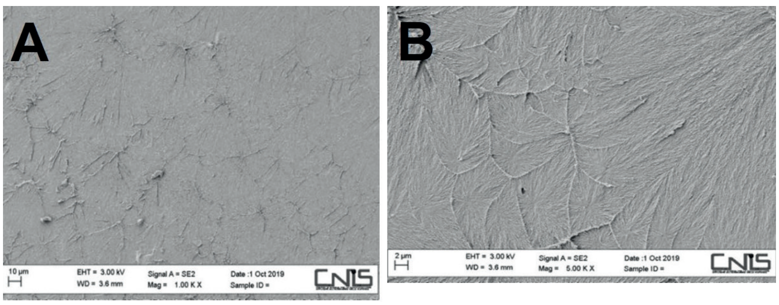

Figure 8. SEM images of PMMA.

inforcement of this material. The graphene sheets determined a greater increase in glass transition temperature (T_g) and in the memory module. An et al[16] and Song et al[17] studied the mechanical properties of a PMMA-based dental composite reinforced with GO incorporated into PMMA by ultrasonic dispersion in liquid phase followed by mechanical milling. The results showed that the presence of GO made PMMA harder and more resistant. Ramanathan et al[18] demonstrated that

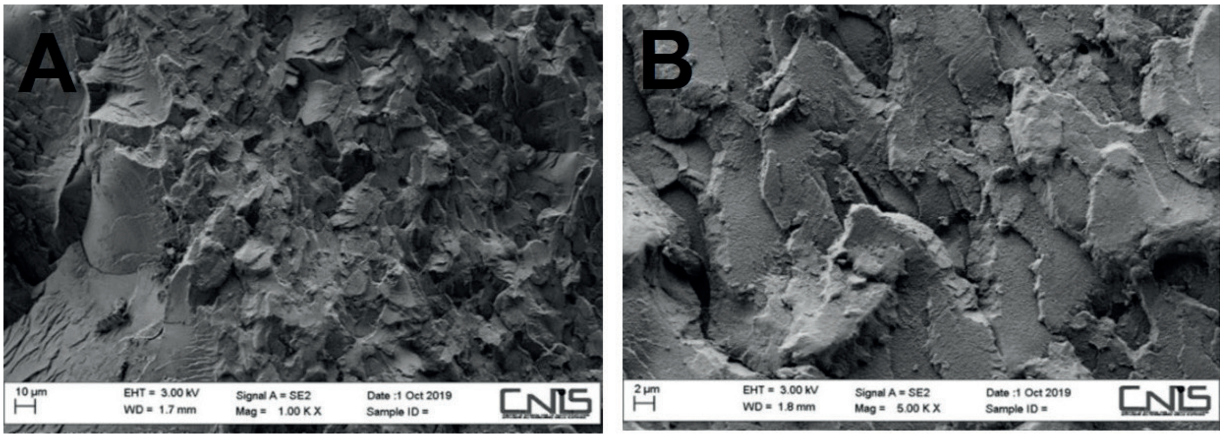

Figure 9. SEM images of G-PMMA.

the addition of 1% of graphene to PMMA leads to an increase of 80% in the value of the EM and of 20% in the value of the tensile strength. Using three-point flexural tests, Lee et al[19] analyzed the antimicrobial-adhesive effects due to the incorporation of graphene-oxide nanosheets (nGO) into PMMA. They found that the addition of 0.5 wt% of nGO into PMMA significantly enhanced the FS and adding more than 0.5 wt% nGO significantly increased the surface hardness. The results of the present study are in line with previous studies. The use of graphene as reinforcement within a nanocomposite showed a statistically significant difference in the values of FS and EM and a greater homogeneity of the mechanical behavior during the bending test.

Conclusions

This study investigated the application of graphene to PMMA to improve flexural strength and elastic modulus values. This new material will be an innovation for the manufacture of dental fixed and removable prostheses, allowing clinicians and dental labs to work in a more predictable way ensuring a better finished product. It was concluded that further investigations are needed to establish the resistance to fatigue of the G-PMMA.

Conflict of Interests

The Authors declare that they have no conflict of interests.

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