

WATER SORPTION, SOLUBILITY AND MONOMER RELEASE OF A FAST POLYMERIZED HEAT-CURING RESIN ENHANCED WITH GRAPHENE SILVER NANOPARTICLES

Cecilia BACALI^a, Marioara MOLDOVAN^b, Stanca CUC^b,
Corina Elena TISLER^{a,*}, Smaranda BUDURU^a

ABSTRACT. Heat-cure denture base resins are the most used materials in denture fabrication for almost a hundred years, because of their favorable characteristics, but they also have some drawbacks that influence the durability and biocompatibility. Over time researchers tried to obtain improvements of the denture materials by adding different types of additives. Water sorption, solubility, and monomer release are among the most important acrylic resins characteristics that influence dentures' durability and biocompatibility. The aim of the present study was to evaluate the effect of graphene silver nanoparticles addition to a commercial heat-curing acrylic resin processed through a fast-polymerization cycle on the water sorption, solubility, and monomer release.

Keywords: *acrylic resin, water sorption, solubility, monomer release, graphene silver nanoparticles.*

INTRODUCTION

Acrylic resins have been used for almost 100 years in denture fabrication without major improvements [1]. Over time, they showed good mechanical and esthetic characteristics, biocompatibility, and low toxicity [2,3] together

^a *Iuliu Hatieganu University of Medicine and Pharmacy, Department of Prosthodontics and Dental Materials, 32 Clinicilor str, 400006, Cluj-Napoca, Romania.*

^b *Department of Polymer Composites, Institute of Chemistry "Raluca Ripan", Babes-Bolyai University, 400294 Cluj-Napoca, Romania*

* *Corresponding author: corina.tisler@yahoo.com*



with easy repairs and low costs. These materials, accessible for the patients, are also convenient for the technicians, which do not need expensive devices in the fabrication process. However, among its shortcomings are some mechanical characteristics such as the brittle nature of the acrylic resins and the low flexural strength that may favor denture fractures and affect durability. The resin surface characteristics and poor antimicrobial activity are factors that favor bacterial adhesion to the denture. Other inconveniences are related to the water sorption, solubility, and monomer release, which can influence the dimensional stability, affecting the material durability [4]. The residual monomer is also related to possible adverse reactions - cytotoxic effects, inflammations of the oral mucosa, and allergic reactions [5]. As regarding the monomer release, although it is well known that in the resin obtention the conversion of the monomer to polymer is not complete [6], it has been demonstrated that fast polymerization methods are associated with higher amounts of residual monomer release compared to the standard polymerization techniques [6,7]. After the polymerization reaction that takes place between the PMMA powder particles and the methyl methacrylate monomer, a certain amount of unpolymerized monomer is always found [7,8].

Some of the acrylic resin characteristics, like water sorption and solubility, need to be improved for better durability and functionality of the acrylic resins [4]. Different materials were added to dental materials over time in order to improve their mechanical behavior and to induce antibacterial properties [9,10,11,12]. Composite materials improved with nanomaterials like graphene oxide showed improved mechanical and physical properties while the weight of the material is just slightly increased [9]. In other studies, antimicrobial effects (*Streptococcus* mutants, *Candida albicans*) were obtained together with improved mechanical properties (flexural strength) when using PMMA composites improved with silver and nano-ZrO. Addition of silver nanoparticles induced antibacterial properties to PMMA to both Gram-negative and Gram-positive bacteria [13,14].

The additives used for the acrylic resin improvements can influence other material properties like water sorption, solubility, and the residual monomer. Water sorption of acrylic resins is determined mainly by the polar properties of the molecules [15] and can be also associated with the porosity of the material [16]. Water sorption, solubility, and monomer release were shown to be influenced by the type of curing method and also by the additives used in the enhanced resins [17,18].

In our country, heat cure resins, such as Superacryl Plus (Spofa Dental) are widely used in removable denture fabrication because of the low costs, ease in processing, and the simple laboratory devices that are needed.

The *aim of this study* is to analyze the effect on the monomer release, solubility, and water sorption of graphene oxide and silver nanoparticles addition to a heat curing resin that was processed in a short curing cycle.

The *null hypothesis* was that there is no difference between the water absorption, solubility, and residual monomer results between the samples of conventional and enhanced heat-curing resin.

RESULTS AND DISCUSSION

Although PMMA resins are used for a long time in the fabrication of removable dentures due to their favorable characteristics, they cannot be considered an ideal material. Many attempts have been made by adding different types of materials in order to improve their mechanical, physical, or chemical properties. The presence of the denture in the oral cavity exposes it to a variety of forces during mastication, while the material is also interacting with oral fluids and different beverages.

Over time, many studies were directed in the research of an ideal material for the denture bases, a material that should have in the same time adequate mechanical, physical, and chemical properties. Various materials, such as fibers and fillers of different types and sizes, have been used to improve the mechanical properties of PMMA [12,19,20] and to enhance its antibacterial activity and biocompatibility. Properties like minimum water absorption, solubility, and low residual monomer are also desired in order to obtain better acrylic resin behavior, durability, and esthetics.

It is well known silver's property to inhibit bacterial growth. Studies demonstrated its biocompatibility and lack or minimal cytotoxicity when used in low concentrations. [10,13]. A lower monomer content can improve material characteristics and also biocompatibility [6].

Graphene has a bidimensional structure of carbon atoms disposed in one – atom thick layer. Graphene oxide can be obtained by graphite oxidation. It has remarkable mechanical properties such as high resistance, flexibility, low weight that permits the material a wide applicability. Mechanical properties of graphene oxide were studied by Forati et al. [9] who demonstrated that small amounts, up to 1%, of graphene oxide, added to polyether sulfone nanocomposite significantly improved the mechanical properties of the material and Kang et al. [21] who found a Young moduli of 695 \pm 50GPa, ultimate tensile strength values 3-33 GPa, while Lee [22] obtained a Young moduli of 1TPa and a breaking strength of 130 GPa, for the graphene monolayer, resulting the strongest material ever measured.

An ideal denture material should have high chemical and thermal stability [15] for better durability and low possibility of side effects. Heat-cure PMMA are the most used materials for denture fabrication [1].

In rapid curing cycles the presence of a low concentration of benzoyl peroxide initiator in the powder and a very small activator dimethyl-p-toluidine in the monomer can reduce the porosity of the acrylic resin [23], and by this way, also the water absorption. In a study that evaluated water sorption and solubility values for self-cured and heat-cured acrylic resins, significant differences were found between mean values of the various acrylic resins, but no correlation was found between the studied properties [15]. The processing methods can influence the water absorption of acrylic resins used in denture fabrication [24].

Superacryl plus is an easy processing, finishing, and polishing heat cure resin, frequently used in our country in complete denture fabrication. It is a modern variant of methacrylate resin, supplied in bicomponent system, powder and liquid, and is recommended for the fabrication of removable denture bases, orthodontic appliances and indirect rebasing of removable dentures. It can be processed, according to the manufacturer, using four types of curing methods: standard polymerization, faster polymerization, fast-boiling polymerization, and polymerization using a pressure polymerizing device. The standard polymerization recommends a total processing time of 2 hours that starts with the flask immersion in cold water, followed by a raising of the temperature to 70 0C and then to 100 0C. The faster polymerization method that was used in our study consists of flask immersion in cold water, followed by a temperature raising to 100 0C, which was then maintained for the next 45 minutes.

A fast-boiling method is also possible, but only for partial dentures; the flask is directly immersed in boiling water, and the temperature (100 0C) is maintained for 45 minutes. The curing method in a pressure polymerizing device is performed in a 10-15 minutes' interval, without flacking, directly on the model, at a pressure of 0.6 MPa and a 100-110 0C temperature; it is though recommended only for small partial dentures. Adverse reactions to this material are possible (methyl methacrylate sensitivity), especially for allergic people. Higher monomer amounts were found in the self-cure resin compared to the heat-cure ones [25]. The level of residual monomer in self-curing denture base materials. The higher amounts of residual monomer can be caused by the graphene oxide inhibitory effect in the polymerization reaction that leads to a lower conversion of the monomer into polymer [26].

1. MMA monomer release

The amount of methyl methacrylate monomer (MMA) was higher when the fillers were added to the studied resin and when the samples were immersed in chloroform, than in simulated saliva, as shown in the **Table 1/Figure 1**.

Table 1. MMA values for MMA release for the M (control), P1(1% G-Ag Np) and P2(2% G-Ag Np) samples stored in chloroform and simulated saliva

MMA -	Chloroform (mg/50ml)	MMA - saliva (ug/g)
M	9.98	0.751
P1	11.268	0.73
P2	12.296	0.66

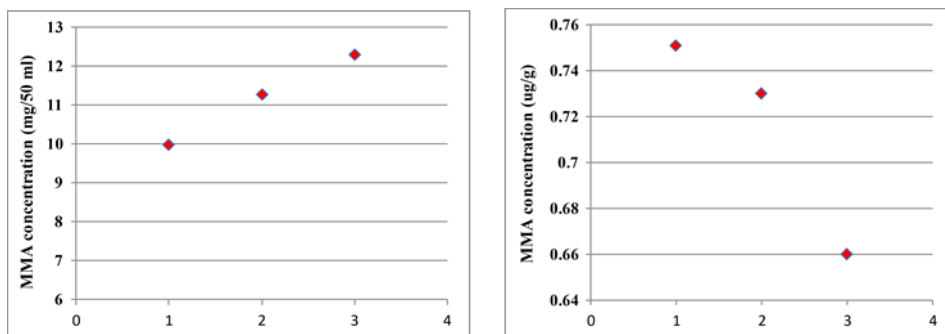


Figure 1. Higher amounts of residual methyl methacrylate monomer (MMA) were obtained for the samples dissolved in chloroform compared to those dissolved in the cell medium solution (figures). The enhanced samples P1 and P2 showed higher values of MMA. Lower amounts of MMA were determined for the samples stored in cell medium.

In the present study the residual MMA was recovered from two types of solvents, cell medium solution, used to simulate *in vivo* conditions [27] and chloroform. The amount of monomer in cell medium solution was lower than that found in the chloroform solution, as a result of methyl methacrylate solubility in chloroform. G-Ag Np addition to PMMA increased the residual monomer dissolved in chloroform solution. The graphene high possibility of interaction may contribute to the incomplete polymerization, due to their interference in the curing process [26].

The amount of the unconverted monomer in the polymerization reaction is important to be assessed because of its possible side effects. The contact with the residual MMA can cause irritations of the skin, dependent on the time of exposure, for the persons which manipulate the material [28], even if they wear dental gloves, as long as vinyl and latex gloves showed monomer permeability [29]. Other adverse reactions concerning the nervous system, headaches, balance disorders and visual disturbances, as a result of vapour inhalation or dermal exposure to methyl methacrylate, were also found [30,31]. The values obtained for MMA resulted from a fast polymerization processing method in this research were higher than those obtained for a self-cure resin in a previous study [32].

Studies showed that a longer curing time can reduce the amount of residual monomer [5]. A 7h immersion in water at 70°C followed by a 1h immersion in water at 100°C are recommended for a maximum conversion of the monomer [33]. The use of microwave polymerization was also showed to reduce the residual monomer content comparing to other polymerization methods [34]. The immersion of the material in water at 37°C for 24 hours is generally recommended after the polymerization reaction in order to reduce the amount of unreacted monomer [35] and also the associated side effects.

2. Water sorption

Water can have in time plasticizing and degradation effects for the dentures, as a consequence of the interaction with the polymer chains and irreversible changes caused in the matrix [4,15]. In the present study, the decrease in water sorption for the higher concentrations of additives may be caused by the filler distribution within the matrix, the lower porosity and the hydrophobic character of graphene. The water sorption seems to be related to the residual monomer, a soluble component of the acrylic resin. Studies show that the processing method [36], the temperature and the time of polymerization reaction can influence the material characteristics (like density, porosity), also the residual monomer, and consequently the water absorption.

The results obtained after the samples storage in distilled water and saliva for 28 days showed a significant weight increase. Higher values of water sorption were obtained for the control sample, both in water and saliva (Table2). A lower water sorption was found for the samples with higher additives content, the lowest value was obtained for the P2 sample. The fillers distribution within the enhanced resin and its lower porosity may have influenced the diffusion of water molecules into the polymeric matrix. No significant variation between samples P1 and P2 were found.

Table 2. Water sorption expressed as weight increase percentage after saliva exposure

Sample	Saliva exposure time	
	7 days	28 days
M	1.24 ± 0.11 ^a	1.49 ± 0.05 ^a
P1	0.94 ± 0.08 ^b	1.31 ± 0.09 ^b
P2	0.81 ± 0.12 ^c	1.26 ± 0.14 ^b

M, PMMA sample; P1, PMMA + 1%GAgNp; P2, PMMA + 2%GAgNp. Different superscript letters indicate statistically significant variation ($p < 0.05$) between the samples

The fast polymerization method may have increased the water sorption, as higher values were obtained than for self-cure resin evaluated in a previous study [32].

3. Solubility

The material weight loss was tested at 37°C during a 28 days interval using two different solvents – water and saliva. The sample mass was weighted after 1, 7, 14, 21, 28 days of immersion [Figure 2].

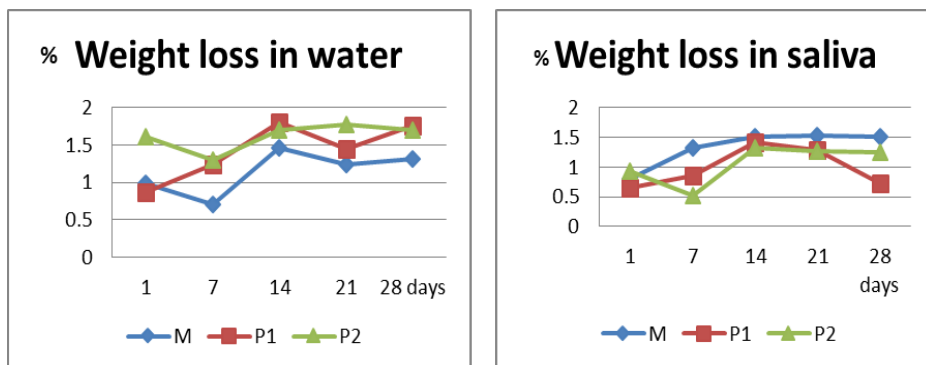


Figure 2. Mean values of weight loss in water and saliva (%) for the control (M) and reinforced samples P1 and P2 after 1, 7, 14, 21, 28 days of immersion

Lower values in terms of weight loss in water were found for the samples with lower content of additives (1%) than for the samples with higher fillers concentration (2%). The control samples (M) showed the lowest weight loss in water, registered after 7 days, from the tested materials. The highest weight loss in water was registered for the P1 sample in the 14th day.

Regarding the weight loss in saliva, the higher values were obtained for the control sample (M), while the enhanced materials (P1, P2) showed slightly lower values. The samples with 2% G-Ag Np showed the lowest weight loss in saliva from the tested samples, registered after 7 days. The highest value for the weight loss in saliva was found for the control sample. Lower values were generally found for the weight loss in saliva than for the solubility in water.

The values were slightly higher than those obtained for a self-cure resin in a previous study [14]. Increased values in solubility can be associated with the higher values of residual monomer and the consequent diffusion of the water and solvent molecules within the resin matrix. The faster polymerization method could cause a lower monomer conversion that can be associated to the higher solubility.

Water sorption and solubility were according to the International Standard Organization (ISO) specifications, which recommend that water sorption should be lower than $32 \mu\text{g}/\text{mm}^3$ for heat-cured or self-cured materials and the loss in mass per unit volume (soluble material) should be lower than $1.6 \mu\text{g}/\text{mm}^3$ for heat-cured and $8.0 \mu\text{g}/\text{mm}^3$ for self-cured materials [37]. There were no correlations between the water sorption and solubility values.

The results obtained in this research are in agreement with the results obtained in other studies on water absorption, solubility and monomer release in acrylic resins [14,15,32].

4. SEM Analyses

Scanning electron microscopy was performed to analyse the surfaces of the samples. Magnification of 500x, 5000x and 10000x were used for capturing conclusive images. The additives have a uniform distribution inside the resin matrix, at both 1% and 2% concentrations. They appear like white areas surrounding the PMMA spheres [Figure 3].

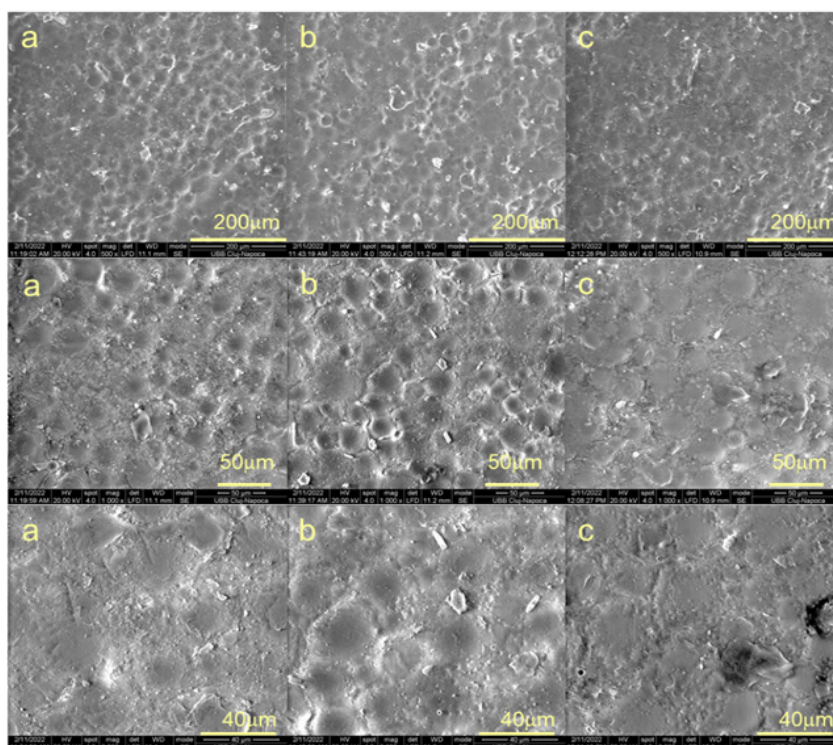


Figure 3. SEM imagines for samples a) M, PMMA; b) P1, PMMA + 1%GAgNp; and c) P2, PMMA + 2%GAgNp.

At the SEM images analysis, a uniform distribution of the additives within the acrylic resin was found, together with a low porosity of the samples. This aspect has a great importance for the material properties, as the higher the homogeneity is present, the lower the water absorption and solubility [38].

The characteristics of new proposed materials are first of all assessed by in vitro investigations, focused on different physical, chemical and mechanical properties [39,40,41].

Limitations. The water sorption and monomer release should also be evaluated for the other Superacryl plus curing methods, in order to evaluate the differences between different polymerization techniques.

CONCLUSIONS

The addition of graphene silver nanoparticles to a commercial heat-cured resin processed by a fast-polymerizing technique show to influence the water sorption, solubility, and monomer release values.

Higher amounts of residual monomer for the enhanced resins in chloroform, but lower in saliva compared to the control samples were found. Lower water sorption values were determined for the samples containing additives (depending on the fillers content) than those of the control samples.

Higher weight loss values in water for the P1 and P2 samples, but lower in saliva compared with M samples were obtained. A uniform distribution of the fillers and a low porosity for the enhanced samples was observed on the SEM images.

The water absorption, solubility, and monomer release values found in the study were in accordance with ISO specifications.

EXPERIMENTAL SECTION

1. Materials

Superacryl Plus (Sofa Dental), a heat-cure commercial acrylic resin used in complete denture fabrication, was used in the study. Addition of 1% and 2% G-AgNp to the resin was performed after the additives' synthesis through Radio-Frequency Catalytic Chemical Vapor Deposition (RF-CCVD) method [11]. Silver nanoparticles were distributed over magnesium oxide (Agx/MgO, where x = 3 wt %) and graphene oxide, using techniques presented in previous studies. The additives were mixed with the denture base resin in

95% ethyl alcoholic solution, at room temperature, under continuous stirring, for 30 minutes and then dried in the oven at 40°C. A methane flow rate of 80 mL/min was used [42]. The reaction interval was 60 minutes [43].

2. Sample preparation

Three study groups (M, P1, P2) were established, each of them containing ten samples, obtained using the faster polymerization method. The first group, M, contained only the commercial resin, while the P1 and P2 groups contain 1wt % and 2wt % graphene-silver nanoparticles respectively.

The mixture obtained from Superacryl Plus powder and liquid was placed in a stick-shaped plaster mold, immersed in cold water, and then cured in boiling water for a total time of 45 minutes, according to the commercial product specifications concerning the fast polymerization technique. The samples were obtained by cutting the sticks (150mm/15mm) in 5x1mm disks using a precision cutting device (Isomet 1000, Precision Saw, Buehler, ITW, Illinois, USA).

3. Methods

3.1. Water sorption

For water and artificial saliva sorption, a disk-shaped mould was used to obtain specimens of 15 ± 1 mm diameter and 1 mm thickness. The discs were dried in a desiccator in the presence of calcium chloride at 37°C for 24 h till a constant weight (m_0) was obtained. The samples were then divided into two groups and then immersed into distilled water and artificial saliva, respectively. Next, the disks were introduced in an incubator for 28 days, at a constant temperature of 37°C. Every day, the samples were removed from the water and weighted after 10 min (m_1), using an electronic analytical balance. The weight changes due to water absorption (W_a) were assessed, using the following equation (1) [44].

$$W_a = (m_1 - m_0)/m_0 \times 100 \quad (1)$$

3.2. Solubility

Solubility is the characteristic of a material to dissolve in a solvent. The reduction that occurs in the mass can be used to determine the water solubility of the material, according to ISO specifications [37].

The changes in the weight values (W) referred to the initial weight were calculated (after the difference between the initial mass m_0 and the final mass m_f of the sample was determined) using the formula

$$W = (m_0 - m_f)/m_0 \times 100.$$

3.3. Residual monomer

The residual MMA was extracted from the storage liquid (water, chloroform) used for samples' immersion. MMA concentration was determined using high performance liquid chromatography (HPLC). A high-performance liquid chromatograph - HPLC (JASCO - 980) was used, equipped with: Intelligent HPLC Pump (JASCO PU-980); Ternary Gradient Unit (JASCO LG-980-02); 3-line Degasser (JASCO DG-980-50); column thermostat (JASCO CO-2060 Plus; UV-VIS detector (UV-975), and ChromPASS software. The standard monomer was Superacryl Plus liquid (cross-linked methyl methacrylate). The analytical reagent for HPLC was acetonitrile. The water used in the study was Millipore ($18.2 \text{ M}\Omega\text{mcm}^{-1}$). *Stationary phase*: LiChroSorb C18 column (25 x 0.46 cm); *Mobile phase*: Acetonitrile: water: $\text{H}_3\text{PO}_4 = 30:70:0.1$, v/v; nm elution rate: 1 mL / min; detection: UV at 220; column temperature: 40°C.

The retention time (9.2 min) was obtained after the injection of standard MMA. Next, from the standard MMA, solutions with concentrations of 31.25-250 $\mu\text{g/ml}$, were prepared in order to be used for the residual MMA determination. The peak values, obtained by UV detection (according to the solutions concentration), associated with the calibration equation, were used to assess the MMA amount.

The first group of samples was immersed in chloroform, and the second group was immersed in cell medium solution for 24 h [27], then freeze-dried using a Lyophilizator (ALPHA 1-4LDPLUS) and after that dissolved in 2ml acetonitrile. The obtained solutions were filtered and introduced in the high-performance liquid chromatograph for the MMA assessment.

3.4. Scanning electron microscopy

The scanning electron microscopy analysis of the fillers and the samples, using a FEI Inspect microscope (SEM-Inspect S, FEI Company, Hillsboro, OR, USA), S model, functional in high-vacuum and low-vacuum, tan accelerating voltage between 200V and 30kV, was performed. The microscope was equipped with CCD-IR infrared inspection camera and backscatter electron detector, with image processing up to 4096×3536 pixels. The images were obtained at a magnification of 500x and 1000x.

3.5. Statistical analysis

One-way ANOVA test (Microsoft Office, Excel) was used to analyse the statistical differences between the obtained values. Tukey test and Pearson correlation coefficient were also used to evaluate the differences between the mean values of each material and between the studied characteristics, respectively.

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