Evaluation of Electrical Characteristics for PMMA-TiO_2 Nanocomposites Used in Dentistry

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In this paper, it is studied the influence of TiO_2 nanoparticles content (0.2-5% wt:wt) on the electrical conductivities and the dielectric constants of poly (methyl methacrylate) (PMMA) nanocomposites used for 3D printing in dentistry. The nanocomposites films, which have been obtained applying the casting method followed by UV exposure, were mounted in a four electrodes cell for the electrochemical a.c. impedance analysis. The experimental data showed that both the dielectric constant and the electrical conductivity increase with increasing amounts of nano-TiO_2 in nanocomposites. However, the change in the electrical conductivity is not significant for less 1% nano-titania added.

Keywords: ac impedance, nanocomposite PMMA - TiO_2, electrical conductivity, dielectric constant, complete denture, stereolithography

Recently, nanotechnologies based on novel systems associating metallic oxide particles with a polymer matrix have achieved unique physical, chemical, antibacterial and mechanical properties that were not possible with the addition of micron-sized particles [1–3].

In the dental field, the polymer poly(methyl methacrylate) (PMMA) has a wider usage due to its remarkable properties such as good esthetic aspect, biocompatibility, relatively good stability in the oral environment, ease use and repair, low cost, moldability. However, several main drawbacks of this material, namely low mechanical resistance [4], great susceptibility to microbial colonization from the highly contaminated oral environment [5], allergic reactions mostly due to leaching of the monomer [6], degradation of the mechanical properties and resistance to wear in aqueous environment, especially in human saliva [7, 8], have attempted to be solved by adding nanofillers and also by improving the manufacturing technology [9].

The highly biocompatible titania nanoparticles have been successfully used lately in stereolithographic complete denture manufacturing [1, 9, 10]. However, despite of the improvements of the antibacterial and mechanical properties and the good clinical results registered, there has been no scientific study about the electrical characteristics of the newly obtained nanocomposite in the very complex and aggressive environment as human saliva.

Saliva, composed mainly of water along with electrolytes such as sodium, potassium, calcium, bicarbonate, magnesium and fluoride, secretary proteins such as amylase, lipase, albumin, PRPs, histatin, lysozyme and mucins, Immunoglobulins, primarily IgA, IgG, IgM and small molecular weight metabolites such as glucose, urea, uric acid, lipids, epidermal growth factor, insulin, serum albumin, etc. [11–13], plays a very important role in maintaining the overall health of the oral cavity [14, 15]. Human saliva has a variable electrochemical potential also influenced by the characteristics of food and beverages ingested [16].

The electrochemical potentials of metallic ions included in the materials utilized in dental restorations are different from the oral cavity mucosa's electrochemical potential, inducing a galvanic cell formation. With increasing of the number of metallic materials introduced in the oral cavity, a greater number of galvanic cells are formed [17, 18]. Values of the flowing currents depend on the electromotive forces of the galvanic cells created and on the resistances of the flux paths. This may cause destruction of material with metallic content and may induce unpleasant feelings and various diseases with complex diagnostics and treatment, especially for elderly patients with poor oral hygiene [19, 20].

Despite of the fact that PMMA is not a potentially electric conductor, when a polymer matrix is filled with a conducting filler, the composite gains a conductivity value of σ. When the loading of the filler is increased such that the volume filler fraction φ reaches a critical value φ_c, a cluster is formed, and the composite becomes conducting [21]. Because of the presence of a conduction, a change from an insulator to a semiconductor may occur with unfavorable consequences for the oral cavity and general health.

Therefore, the aim of the present study was to assess the electrical characteristics of the nanocomposites (PMMA-TiO_2) with different content of nano-filler in artificial saliva. The research hypothesis was that nano-TiO_2 content could influence the insulator property of the denture base material.

Experimental part

The nanocomposite materials PMMA–TiO_2 were obtained by adding various weight percentages of nano-filler: 0.2, 0.4, 0.6, 1.0, 2.0, 2.5 and 5 to the polymeric matrix, poly (methyl methacrylate) - PMMA. The used chemicals were as follows: PMMA polymer mixture used for 3D printing procedure (eDent 100, Envision TEC GmbH, Germany), TiO_2 (anatase, Aldrich, Germany), isopropyl alcohol (Aldrich), deionized water (125μS), salts: KCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 2H_2O$, K_2HPO_4, KH_2PO_4 (Aldrich-Merck), NaOH (Aldrich-Merck), sodium carboxymethyl cellulose

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(Aldrich) and methyl-p-hydroxybenzoate (Aldrich). The nanocomposites have been obtained according to the procedure presented elsewhere [22]. Upcoming the preparation stage of the nanocomposites, a simple casting method followed by UV curing has been applied. The thoroughly mixed PMMA with nano-TiO_2 dispersed in isopropyl alcohol were cast on a PTFE support and then dried for 4 h at 110^{0}C. After cooling in desiccator, the cast nanocomposite films were cured for 1.5 min under UV light (UV lamp with λ=378-388 nm) for complete polymerization / reticulation of the polymeric matrix. From the resulted films, discs have been cut (with a surface of 1.76 cm^2, and a width of 0.2 cm), and subsequently mounted, in a four electrodes (Ag/AgCl) cell (fig. 1) using artificial saliva, as electrolyte [23].

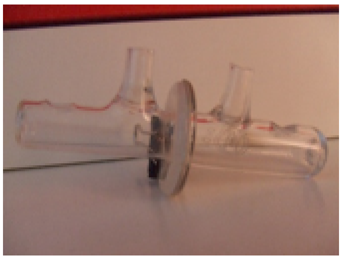

Fig. 1. Four-electrode cell for a.c. impedance measurements

The *p*H of the electrolyte with the composition presented in table 1 was adjusted at 7.2 using NaOH solution.

Table 1
ARTIFICIAL SALIVA COMPOSITION

Chemical compound	Concentration
KCl	8.38 x10^{-3} mol/L
$CaCl_2 . 2H_2O$	1.13 x10^{-3} mol/L
$MgCl_2 . 2H_2O$	0.29 x10^{-3} mol/L
K_2HPO_4	2.40 x10^{-3} mol/L
KH_2PO_4	1.1 x10^{-3} mol/L
Na carboxymethyl cellulose	10.00 g/L
Methyl-p-hydroxybenzoate	2.00 g/L

The *p*H value of prepared electrolyte was verified using a Cyberscan PCD 6500 equipment (Eutech Instruments, METEX Corp. Ltd., USA) and its corresponding combined pH electrode. The electrical characteristics have been studied using an electrochemical combine (Parstat 2273, Princeton Applied Research, USA), at room temperature, for a frequency range between 2.0 MHz and 1Hz, at 10 mV for ac amplitude modulation. The overall electric characteristics of the system were associated with an equivalent electrical circuit. By determining the bulk resistance of the films, the conductivity and the dielectric constant [24, 25] have been calculated for each nanocomposite and then correlated with the nano-TiO_2 added.

The surface morphology and elements dispersion for the nanocomposite films obtained have been investigated with scanning electron microscopy (SEM) technique, using an Oxford Instruments equipment.

Results and discussions

The electrical characteristics of the nanocomposites (PMMA-TiO_2) have been studied for a frequency range 2x10^6-1Hz. Some of the Nyquist plots that were recorded are presented in figure 2. It was observed that the Nyquist diagrams are not significantly modified for a contents of nano-TiO_2 ranging between 0.2 - 0.6% in weight percentages. The differences occurred when the nano-filler amount reached 1%, and even then, the differences recorded were reduced.

Further additions of nano-titania filler resulted not in a dramatic change of the recorded values, but in a modification of the system behavior. Thus, for 2.5% nano-TiO_2 added to PMMA matrix, another semicircle in the high frequency range appeared. This tendency has been observed from the composition with 1% TiO_2 (fig. 2c).

If initially for lower nano-filler contents, the assigned equivalent electrical circuit consisted of a simpler circuit (fig. 3.a.), a more elaborated circuit has to be use to model the nanocomposite behavior for nanocomposites with higher nano-titania content. The capacitive element, C_{dl}, in parallel with another resistance (R_1) has to be introduced (fig. 3b) following the appearance of inhomogeneity within

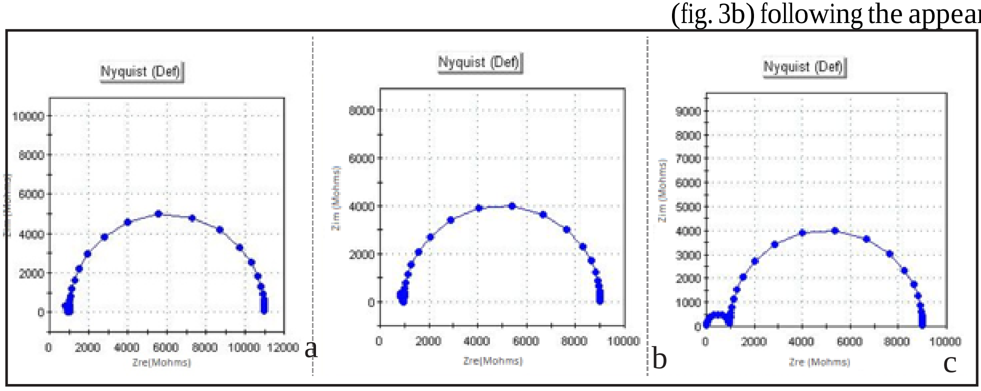

Fig. 2. Nyquist diagrams for: a) 0.4% nano-TiO_2 in PMMA; b) 0.6 % nano-TiO_2 in PMMA; c) 1.0 % nano-TiO_2 in PMMA

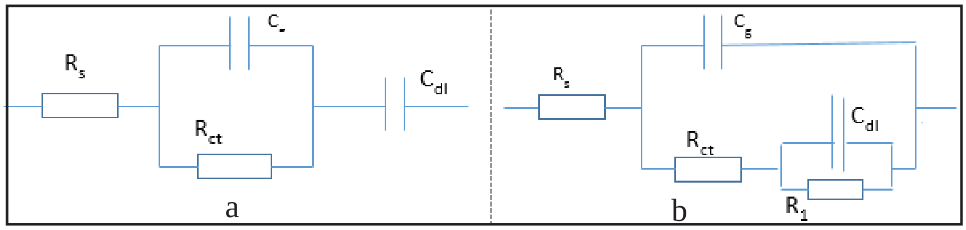

Fig. 3. Equivalent circuits applied to model the electrical behavior of nanocomposites:
a)lower (less 1%) and b) higher (above 1.0 %) content of TiO_2 nanoparticles in PMMA.
R_s = electrolyte solution (artificial saliva) resistance; R_{ct} = charge transfer resistance; R_1 = electrical resistance due to surface inhomogeneity; C_{dl} = diffuse layer capacitance; C_g = geometrical capacitance.

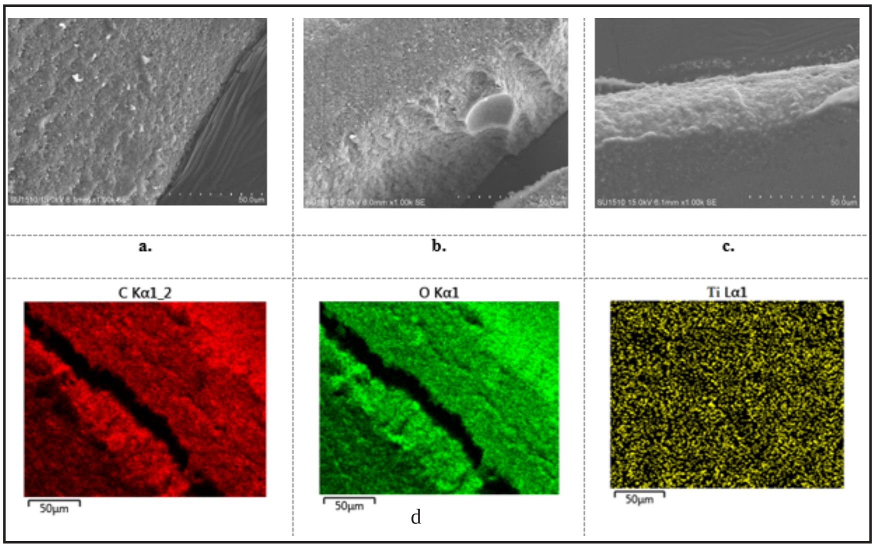

Fig. 4. SEM images of nanocomposites of PMMA with:
a. 0.4%TiO_2 nanoparticles; b. 1% TiO_2 nanoparticles; c. 2.5% TiO_2 nanoparticles; d. distribution of elements for composite PMMA- 0.4% TiO_2 nanoparticles

the nanocomposite structure. It is known that for organic nanocomposites electrical parameters characteristics from the electrical equivalent circuits depends on the surface area [26], an important parameter being S, the geometric area of the analyzed sample. Therefore, any significant change at the surface level of the material could result in a modified behavior. Although the introduction of a titanium oxide nano-filler into the PMMA matrix could improve the dielectric properties, it should be taken into account that the particles tend to agglomerate due to either a limited compatibility with the polymer, or to their cohesive action.

The aspects revealed by scanning electron microscopy (SEM) sustain the previous mentioned electrical behavior of the nanocomposite films, which could be correlated with the nanocomposite surface inhomogeneity evolution. In figure 4 micrographs for some of the prepared nanocomposites are presented.

When the content in nanoparticles increases from 0.4% to 2.5% and then to 5% the surface of the films is gradually changing becoming less and less smoother and homogeneous. For larger amount of nanoparticles a good dispersion of titania into polymeric matrix, as observed for 0.4% TiO_2 nanocomposite (fig. 4d), was no longer present. On the other hand, it is known that there are few factors influencing the titanium oxide nanoparticles dispersion into PMMA, as would be the forces (Van der Waals or hydrogen bonding) between the nano-filler particles. However, an increased amount of titanium dioxide in the considered polymeric matrix lead to a rough surface with a direct influence on the electrical behavior of the composite.

The electrical resistance (bulk resistance) of the PMMA/nano-TiO_2 composite films against the nano-TiO_2 content presented a clear modification, although not very important for lower contents in nanoparticles. The insulating property of the PMMA film without nano-filler makes its electrical resistance out of the measurement range, 10^5 MHz. When adding TiO_2 nanoparticles the electrical resistance decreases as follows: for 0.4% to 7.7 x 10^3 MΩ; for 0.6% to 5.6 x 10^3 MΩ; for 1.0% to 4.8 x 10^3 MΩ. However, the incorporation of 2.5 wt. % nano-TiO_2 and 5 wt. % nano-TiO_2 into PMMA matrix lead to an important decrease of the electrical resistance to about 4.3 MΩ respectively 0.71 MΩ. Such reduced electrical resistance could be clearly attributed to a larger content if TiO_2 nanoparticles, as these nanoparticles represent the conductive material introduced in the obtained nanocomposites films. It is expected that an increased content of TiO_2 enhance the conductive behavior of the nanocomposite following the decreasing of the electrical resistance.

The Nyquist diagram offers the possibility to calculate the geometrical capacitance (C_g in fig. 3) of an equivalent electrical circuit modelling the nanocomposites' film behavior [3]:

$$C_g = \frac{2\pi\upsilon}{R_{ct}} \tag{1}$$

C_g stands for geometrical capacitance while R_{ct} (R_{ct} in fig. 3) stands for charge transfer resistance and n represents the frequency corresponding to the maximum point on the recorded diagram. The BODE plots are important in determining correctly the frequency, ν, and following the nanocomposites electrical behavior.

Due to the dependence of the geometric capacitance on the film dielectric constant according to the following formula (2), it is possible to determine the dielectric constant as time as C_g is known. In the below equation:

$$C_g = \varepsilon_0\, \varepsilon_r \frac{S}{l} \tag{2}$$

ε_0 is the water dielectric constant (ε_0 = 78.5), e_r is the film's dielectric constant, S is the surface (1.76 cm^2) and l is the width (0.2 cm) of the nanocomposite film. The dielectric constant of each nanocomposites has been evaluated against the TiO_2 nanoparticles content, (fig. 5). The graphical representation in figure 5 shows the variation of the dielectric constant value as the nano-titania weight percentage varies, putting in evidence the jump of its value ($\varepsilon_{5\%}$ = 6.9) when the content of nanoparticles is 5%. It is likely that below 2.0% nanoparticles in composite ($\varepsilon_{2\%}$ = 4.2) these conductive particles could be separated from each other into the polymeric matrix and therefore, the insulating PMMA's conductivity is dominant (ε_{PMMA} = 3.2).

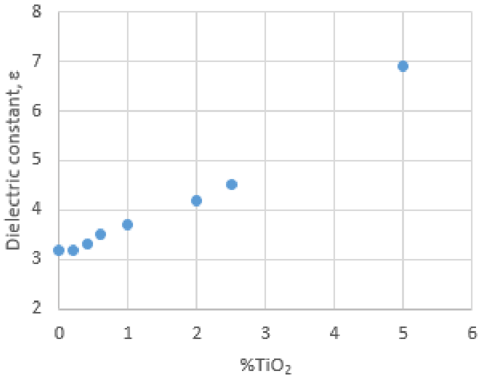

Fig. 5. Variation of dielectric constant as function of nano-TiO_2 content

This could be the reason for which the determined values of the dielectric constant are quite close to the specific value of the initial polymeric matrix ($\varepsilon_{0.2\%} = 3.2$, $\varepsilon_{0.4\%} = 3.3$, $\varepsilon_{0.6\%} = 3.5$). The variation of the dielectric constant for the obtained nanocomposites with the TiO_2 content presented in figure 5 put in evidence that the dielectric constant increases with increasing amount of TiO_2 nanoparticles. Such behavior could be assigned to a larger number of carriers (electrons). Much more, this results in an increase of the electrical conductivity of nanocomposite films.

Measuring the diameter of the semicircles allow us to determine the dc-conductivity, σ, of the nanocomposites from the relation:

$$\sigma = \frac{1}{R_p\left(\frac{S}{l}\right)} \qquad (3)$$

where S is the area of the nanocomposite film sample, l is its thickness and R_p is the equivalent resistance of the parallel circuit.

In figure 6 is presented the evolution of the electrical conductivity of the samples under study as function of the content in nano-titania. It is easily observed that the value of the electrical conductivity is slightly increasing with increase of the concentration of nano-titania, which could be assigned to an increased numbers of charge carries. The conductivity of the initial material used as polymeric matrix (PMMA) presented a conductivity of 10^{-14} $(\Omega.cm)^{-1}$, such value suggesting the behavior of an insulator. Although, that even for low nano-titania content the electrical conductivity increases, the calculated values (around 10^{-12} $(\Omega.cm)^{-1}$) are still consistent with an insulator behavior. It is known that a sharp increase in electrical conductivity is emerging when a certain filler amount reaches a critical content. Such phenomena, the percolation transition, allows a material to pass from insulating to conducting behavior [27]. This is why, it is important to establish if our experimental studies on the considered PMMA-TiO_2 nanocomposites would evidence such situation.

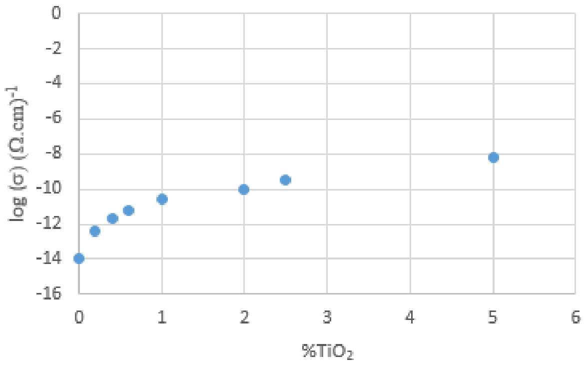

Fig. 6. Variation of electrical conductivity as function of nano-TiO_2 content

As mentioned, for any dental device, and particularly dentures, it is compulsory to work with insulating materials. The presence of different metallic elements in dental restorative materials performs as electrodes with different potentials inducing galvanic effect due to the conductive environment of the oral cavity [28]. Many studies considered a galvanic current of 5μA in the oral environment as the limit of pathological values [29–31].

In vitro studies of short-term exposure of cells to electromagnetic fields at frequencies of 100 Hz or less and at low field intensities have reported important influences on cell physiology with effects on DNA, RNA and protein synthesis, cell proliferation, cation fluxes and binding, immune responses and membrane signal transduction [32]. Long-term electromagnetic field exposure leads to a chronically increased level of free radicals and could determine a higher incidence of DNA damage and therefore to an increased risk of tumor development [33].

The action of the galvanic current may also manifest itself as morphologic changes of oral tissues leading to the development of inflammation of the oral mucosa and the tongue, paresthesia, glossodynia, stomatodynia, neuralgia, etc. [34]. An electric current may also manifest its effects in mucosal changes, and an extensive contact of the complete denture with electrical conductivity to the oral mucosa could lead to significantly structure damage and mucositis [35].

The experimental data recorded in our study and the electrical characteristics calculated did not put in evidence any percolation transition, the nanocomposites preserving their insulating capacity.

Our results show that the increase of the electrical conductivity, even up to $6.3x10^{-9}$ $(\Omega.cm)^{-1}$ for 5% content in nano-titania, still maintain the insulating properties of the material. We could conclude that the added titania (up to 5% in mass) is not leading to the formation of a conductive network inside the composites. In other words, no threshold for the transition from insulator to semiconductor behavior has been recorded.

The following diagram, (fig. 7) aims to present synthetically the overall evolution of the main electrical characteristics followed up in our experiments. The correlated evolution of the studied parameters could be observed. A slightly increasing variation for the dielectric constant up reaching the 5% nanoparticles concentration in nanocomposite was noticed. The decreasing in the electrical resistance is more significant from 1% TiO_2 nanoparticles content. Consequently, the electrical conductivity is increasing, being recorded a similar trend - a more important variation from 1% of titatnia nano-filler introduced into the PMMA matrix (on diagram it is represented -log (σ) for a unitary representation of the calculated data and an easier interpretation).

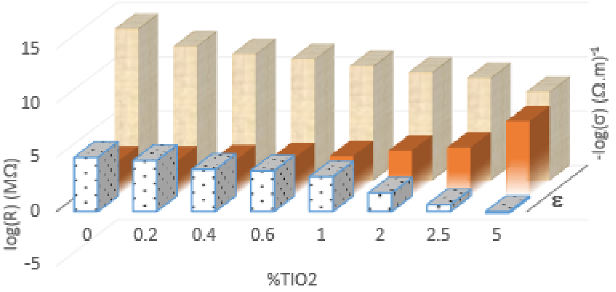

Fig. 7. Variation of electrical resistance (dotted-blue), electrical conductivity (dark-yellow) and dielectric constant (brown-red) of PMMA-TiO_2 nanocomposites against the nanoparticles concentration

The picture of the investigated parameters suggests that the nanocomposites could be used without any specific constraints from electrochemical point of view.

Conclusions

The electrical parameters - resistance, dielectric constant, electrical conductivity, of PMMA nanocomposites with TiO_2 nanoparticles are influenced by the percentage of the added filler. However, these electrical characteristics of the studied nanocomposites were not significantly affected by adding lower nano-titania concentrations. The dielectric constant determined from experimental data presented a slow increase for low additive amount.

Significant variation for the dielectric constant has been recorded for the nanocomposite with 5% titanium oxide nanoparticles, namely 6.9. The other determined values of the dielectric constant are close to the specific value of the PMMA matrix (3.2). The electrical conductivity of nanocomposites was slightly increasing with increase amounts of nano-titania, although none of the determined values overpassed 10^{-9} $(\Omega.cm)^{-1}$, thus the material remaining within the insulators domain. Studying the recorded data, we could conclude that at the optimal concentration of 0.4% TiO_2 nanoparticles in PMMA matrix as previously suggested by us [2], the material preserves its insulating properties, thus underlining the correct choice of the nanocomposite for the *3D printed denture* manufacturing.

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