Could the Old Poly(methylmethacrylate) Face Arrising Challanges of New Advanced Technologies for Dental Prosthesis Manufacturing?

EUGENIA EFTIMIE TOTU[1], CORINA MARILENA CRISTACHE[2]*

[1]University Politehnica of Bucharest, Department of Analytical Chemistry and Environment Engineering, Faculty of Applied Chemistry and Materials Science,1-7 Polizu Str.,1,Bucharest, Romania

[2] Carol Davila University of Medicine and Pharmacy, Faculty of Midwifery and Medical Assisting, 8 Eroilor Sanitari Blvd., 050474, Bucharest, Romania

The biocompatibility, relatively low cost and excellent aesthetic appearance of polymer Poly(methyl methacrylate) (PMMA) makes it the material of choice for fabricating partially and complete dentures. Nowadays the emerging 3D printing technique imposed itself as reliable solution for obtaining dental devices. However, extensive usage of such technique is still limited due to the materials available. Despite PMMA's drawbacks, mainly related to bacterial contamination, wear and mechanical failures, composite polymeric matrix has issued high interest lately. An important improvement in basic material properties have been achieved due to the inclusion of nanosystems, either nanoparticles or nanotubes. The newly shown versatility of reinforced PMMA sustains it as the best alternative for stereolithography (3D printing) technique. This paper highlights the improvements of PMMA by adding different type of nanofillers. Therefore, prospective randomized clinical in vivo studies with the use of biocompatible tested modified filled PMMA and modern technologies should be performed.

Keywords: PMMA, complete denture, Nanofillers, 3D printing

Due to the actual trend of geriatric population growing, there is an increase in the percentage of patients having edentulous or partially edentulous jaws with a constant need of new biocompatible materials and modern technology for re-establishing function and improving quality of life.

For edentulous patients, restorative prosthetic treatment with removable poly(methyl methacrylate) (PMMA) dentures is widely utilized to overcome the loss of all teeth [1]. The biocompatibility with the body environment, relatively low cost and excellent aesthetic appearance of PMMA makes it suitable for fabricating dentures. However, many drawbacks were recorded, these being mainly related to bacterial contamination, wear and also mechanical failures, leading to crack and fractures during clinical use [2].

Despite the fact that there were no essential changes in PMMA formulation since its initial introduction, more than forty years ago, composite polymeric matrix has issued high interest lately because an important improvement in basic material properties have being achieved due to the inclusion methodology of nanosystems, either nanoparticles or nanotubes.

Much more, the polymer nanocomposites proved to be the ideal solution for obtaining the desirable compounds for specific applications either in industry or in medical area [3].

Furthermore, reactions like grafting, cross-linking and blending of polymers with nano inorganic fillers to overcome certain disadvantages such as low mechanical resistance, radio-opacity, bacterial contamination, have been extensively investigated for many years [4-7]. Introduction of nanofillers, even in a few weight percent, onto polymeric matrix have a strong impact on the macroscopic characteristics of the polymer. Some properties such as mechanical, anti-bactericidal or optical properties are dramatically enhanced [4, 8-10].

This article will address the improvements of poly(methyl methacrylate) (PMMA) for removable dentures use by adding different type of nanofillers in the view of its usage for new manufacturing techniques.

Experiemntal part

Poly(methyl meta acrylate) or according to IUPAC Poly(methyl 2-methylpropenoate) could be produced through the methyl metacrylate monomer radical polymerization [11]. It represents a quick and inexpensive alternative for verifying the functionality and adapting a specific medical device to the working model.

PMMA is recommended for extensive use in medical field due to its aesthetic aspect, transparency as well as low cost. As there are specific requests according to the application intended, PMMA could be modified in order to assure an enhanced chemical resistance, the sterilization with gamma rays, a complete biocompatibility, etc. It has

* email: corinacristache@gmail.com

to be mentioned its behavior as good electrical insulator and the low absorbance of humidity when exposed in liquid electrolytes.

Drawbacks of PMMA Iin dental applications

Poly(methylmethacrylate) (PMMA) is one of the oldest and most commonly organic materials used in dentistry. Among its employments in dentistry, for temporary crowns, orthodontic appliances, individual trays, etc., has become a common material for producing denture bases [12] and artificial teeth in clinics due to its various advantages: biocompatibility, excellent esthetic appearance, stability in the oral environment, ease to use and repair, with relatively low cost and also due its tasteless and odorless properties, etc.

However, there are several drawbacks of PMMA as denture base material to be addressed.

Mechanical resistance

Fracture of acrylic resin dentures is still a common clinical occurrence, between 57 and 64% of all failures of removable dentures [13-16]. Denture fracture inside the mouth due to: anatomical characteristics involving a customized design such as severe frenal notch, prominent torus palatinus [10], poor fit of denture base [10, 17]. A faulty fabrication, not according to the manufacturer recommendation may lead to insufficient mechanical properties of the denture base resin and failure during service[18]. In addition, excessive biting force or bruxism may also cause fracture [19, 20]. Denture fracture outside the mouth occurs from impact caused by accidents as a result of expelling the denture from the mouth while coughing or dropping the denture [10]. Several studies [21, 22] reveal that mechanical and tribological properties of PMMA, especially hardness and wear are of primary concern in fabricating dentures [23-25].

Bacterial contamination

Denture base is susceptible to microbial colonization from the highly contaminated oral environment [26]. The absence of ionic charge in the PMMA denture base prevents the adsorption of salivary defense molecules [27-29] on the denture surface and favors biofilm formation[30]. Other mechanisms favoring bacterial adherence include hydrophobic interaction[31], electrostatic interaction[32], and mechanical attachment. Several important local factors to be mentioned are porosity, surface roughness, poor denture hygiene (especially for geriatric patients with limited dexterity), and continual and nighttime wearing of dentures. *Candida* species - especially *C. albicans[33]* - are found in the oral cavity of 60–100% of denture wearers[34] and are among the most common etiologic agents causing fungal infections[35] - denture stomatitis.

Lack of radio-opacity

Denture bases constructed from pure PMMA are not radiopaque, and thus they are not detectable on radiographs. Radio-opacity of denture bases is a desirable attribute because should such denture be accidentally

Table 1

ADDITIVES UTILIZED TO IMPROVE PMMA CHARACTERISTICS FOR DENTURE BASE MANUFACTURING

Fillers added	Characteristics	Type of study	Reference
ZrO_2 nanotubes	A dose of 2.0 % by weight untreated ZrO_2 nanotubes conferred the best reinforcement effect	In vitro	Yu et al. 2014[48]
Silica nanoparticles	0.023% nanosilica contents superior mechanical properties	In vitro	Balos et al. 2014[50]
Aluminum oxide (Al_2O_3) powder	2.5 % Al_2O_3 by weight powder significantly increased its flexural strength and hardness with no adverse effects on the surface roughness.	In vitro	Vojdanier al.2012[51]
Metal fillers (aluminum and silver) concentrations 10%, 20%,and 30% by volume	Improved tensile and flexural strengths were observed in PMMA with only 10% and 20% silver fillers and 10% aluminum fillers.	In vitro and in vivo (10 patients)	Yadav et al.2012[42]
Aluminum oxide (Al_2O_3) powder	Incorporating Al_2O_3 powder from 5 to 20% by weight into conventional heat polymerized denture base resin, resulted in an increased thermal diffusivity, which ensured a better perception of temperature changes	In vitro	Atla et al. 2013[52]
Silver colloidal nanoparticles	PMMA/Ag containing 5% silver colloidal nanoparticles had good efficacy against *C. albicans*,	In vivo	Monteiro et al. 2012[53]
Silver nanoparticle (NPAg) solution	After incorporated into the denture base acrylic resin, no effect on the *C. albicans* adherence and biofilm formation was detected, regardless of the AgNPs concentrations	In vivo	Wadi et al.2012[54]
Silver nanoparticles (AgNP) coating	Inhibition of *Candida species* adherence to the denture material surface	In vitro	Kamikawa et al. 2014[55]
PMMA mixed with 5 % by weight nanosilver	Improving the thermal conductivity and compressive strength of PMMA	In vitro	Hamedi-Rad et al. 2014 [56]

continuated table 1

Diamond-like carbon (DLC) thin films doped and undoped with silver nanoparticles coating	DLC thin films significantly diminished *C. albicans*biofilm formation on the resin surface compared with the control group	In vitro	Queiroz et al. 2013 [57]
2%, 4%, 6%, 8%, 12%, 16% and 20% by weight seashell nanopowder	Wear resistant increased and least frictional force is observed on addition 12% seashell nanopowder reinforced composite	In vitro	Rajkumar et al. 2014[49]
Nitrile butadiene rubber (NBR) particles mixed with treated ceramic fillers (aluminum oxide, yttria-stabilized zirconia, and silicon dioxide) were used to reinforce PMMA denture base material	The impact strength and fracture toughness improved significantly ($p < 0.005$) when compared with unreinforced PMMA matrix.	In vitro	Alhareb et al. 2015[58]
PMMA-modified hydroxyapatite (M-HAP) prepared by adding HAP whiskers up to 15%	The mechanical properties of the prepared denture base samples were enhanced greatly after incorporating with M-HAP fillers	In vitro	Pan et al. 2013[59]
Methacrylic acid (MA) and functionalized TiO_2 nanoparticles	Improved mechanical properties	In vitro	Khaled et al. 2007 [60]
PMMA mixed with 5% Al_2O_3/ZrO_2.	Addition Al_2O_3/ZrO_2 in PMMA improves the mechanical properties of denture base material.	In vitro	Alhareb et al 2010[58]
Acrylic resin containing nanoparticles TiO_2, SiO_2 concentration of 1% and 0.5%	Adding $NPTiO_2$ and $NPSiO_2$ to acrylic resins for antibacterial effect. NP addition reduces the flexural strength of the final products, and this effect is directly correlated with the concentration of nanoparticles	In vitro	Sodagar et al. 2013 [61] Nazirkar et al. 2014[62]
0-5%TiO_2 nanotubes (n-TiO_2)	Proved that 3% n-TiO_2 enhanced mechanical properties	In vitro	Dafar 2014 [5]
TiO_2-coating / spray-coating technique	Good biocompatibility. Self-cleaning and antibacterial denture properties. Bio-effects: no irritation or sensitization of the oral mucosa, skin or intracutaneous tissue	In vivo: hamster (oral mucosa), guinea pig (skin), rabbit (intra-cutaneous test)	Tsuji et al. 2015 [6]
	Increase the surface glossiness. No influence on base material color.	In vitro	Mori et al. 2015 [63]
	Photoinduced antibacterial effect: Staphylococcus aureus (gram positive) and Escherichia coli (gram negative)) are inactivated within 2 h illumation	In vitro	Su et al. 2010 [4]

inhaled or swallowed, it should be detected by radiographic means. Any delay in localizing or removing the foreign body may be life threatening [10].

Water absorption

Exposure of the denture base to an aqueous environment is known to degrade their mechanical properties and resistance to wear [36, 37]. These deteriorations have been attributed to the hydrolytic degradation of the polymer matrix and filler, as well as to the water-induced filler-matrix bond failure [38-40].

Thermal perception

Low thermal conductivity compromises the patient's appreciation of taste by not conducting hot and cold sensations [41, 42]. Moreover, a lack of thermal stimulation to the underlying mucosa may result in reduction of its thickness, especially that of stratum corneum, predisposing the mucosa to injury caused by dentures functioning [42]. It is therefore desirable to make the denture base thermally conductive [43], as it may serve to maintain the health of the underlying mucosa and also for a better appreciation of taste and improving quality of life.

Results and discussions

PMMA reinforcement content

Developing composites using different fillers with Poly(metylmethacrylate) [24, 44-47] lead to finally improved denture base and/or artificial teeth [48]. Such experimental works supposed to use as additives: fibers, whiskers or nanoparticles as presented in table 1. The PMMA bio-composites with 0, 2, 5% filler percentages are the most common compositions used resulting in an uniform filler's disperse in the polymer, although 6% or 12% additive could be as well applied - for seashell nanopowder [49].

The antibacterial action under ultraviolet light [64] of TiO_2 particles as well as their proved biocompatibility sustain titania as important nanofiller for polymers of medical usage.

In the perspective of obtaining a functional composite PMMA/TiO_2 either by melt or solution mixing of PMMA and TiO_2 nanoparticles, very useful proved to be the presence of various coupling agents in order to assure a good dispersion of TiO_2 nanoparticles [8, 60, 65- 80]. A poor dispersion of the filler into the polymeric matrix could result in an inappropriate composite material for dental usage [81]. Also, failure in obtaining performing composites has been assigned to an inappropriate TiO_2 nanoparticles' dimension and the lack of interaction between the polymeric matrix and the nanofiller [82]. For example, a successful coupling agent is the methacrylic acid [83, 84] which allow TiO_2 binding to PMMA skeleton at room temperature. It was observed that an increase amount in titania nanoparticles resulted in improved thermal and mechanical characteristics for PMMA, transforming this *old* polymer in a suitable material for modern dental technologies [85, 86]. It is well-known that the PMMA based dental devices are actually facing a common mechanical failure [23, 87, 88] that could be overcome using reinforced PMMA with metallic fillers [89]. Practical usage in clinical environment of PMMA or PMMA composites put the material under important mechanical stress [89-91]. Following the masticator function action, PMMA dental devices are deteriorated in time. As consequence, new solutions have been introduced, as PMMA high-pressure polymerization [14]. Thus, obtaining a better mechanically resistant material, it was possible to use it in the new manufacturing techniques of dental prostheses. The tremendous advance of microelectronics and software technology allowed to pass an important threshold in dental devices manufacturing towards the digital era through Computer Aided Design and Computer Aided Manufacturing applied in dentistry. Much more, going further in advanced technology, nowadays the emerging 3D printing technique imposed itself as reliable solution for obtaining dental devices [92]. However, the extensive usage of such technique is still limited due to the materials available. The above shown versatility of reinforced PMMA sustains it as the best alternative for stereolithography (3D printing) technique.

Conclusions

Although removable dentures are usually less appreciated due to concerns regarding their comfort, aesthetics, masticatory function, occlusal stability and maintenance of oral hygiene, it still remains a viable and predictable treatment choice in clinical dentistry [93].

Some of the new trends, as previously shown, includes PMMA denture base improvement by using various additives/filler, especially TiO_2 based leading to better recorded performance [94]. Not only dental materials need to be improved but also the manufacturing technique and the use of computer-aided design/computer-aided manufacturing (CAD/CAM) technology [95, 97] will lead to simplification of the laboratory work, shorten chair times and increases treatment's quality.

The fabrication of complete dentures using improved PMMA especially by adding TiO_2 nanoparticles and by using CAD-CAM technology (milling or 3D printing) is considered a promising field for future research. We can conclude that prospective randomized clinical in vivo studies with the use of biocompatible tested modified titanium dioxide filled polymers and modern technologies are needed.

Acknowledgements: Funding: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCDI- UEFISCDI, project number 30/2016, within PNCDI III.

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Manuscript received: 3.10.2016