Effects of coating with different ceromers on the impact strength, transverse strength and elastic modulus of polymethyl methacrylate

Esma Başak GÜL¹, Mustafa Hayati ATALÀ¹, Bekir EŞER¹, Nilüfer Tülin POLAT¹, Meltem ASİLTÜRK² and Ahmet GÜLTEK³

¹ Department of Prosthodontics, Faculty of Dentistry, İnönü University, Malatya, Turkey
² Department of Materials Science and Engineering, Akdeniz University, Antalya, Turkey
³ Department of Chemistry, Faculty of Arts and Science, İnönü University, Malatya, Turkey
Corresponding author, Esma Başak GÜL; E-mail: ebasakgul@gmail.com; esma.gul@inonu.edu.tr

The aim of this study was to evaluate the mechanical properties of polymethyl methacrylate (PMMA) after coating with different ceromers. For transverse strength and modulus of elasticity tests, specimens of 65×10×2.5 mm dimensions were prepared (5 groups, n=10). For impact strength test, specimens of 60×7.5×4 mm dimensions were prepared (5 groups, n=10). Test group specimens were coated with one of four different types of ceromers, and specimens in the control group were not coated. After specimens were tested for transverse and impact strengths, the data were analyzed with Kruskal-Wallis and Conover post hoc tests (p<0.05). GLYMO-TEOS-TiO₂ and A174-TEOS significantly increased the transverse strength of PMMA. All ceromers caused a statistically significant increase in the elastic modulus of PMMA. While GLYMO-TEOS-ZrO₂ significantly decreased the impact strength, the other ceromers did not cause any statistically significant difference in impact strength. Coating with ceromers substantially improved the mechanical properties of PMMA.

Keywords: PMMA, Reinforcement, Coating, Ceromers, Mechanical properties

INTRODUCTION

Polymethyl methacrylate (PMMA), a non-resorbable polymer, is made up of a flexible backbone of carbon-carbon chains with pending methacrylate groups¹. PMMA is widely used as a denture base material due to the desirable properties of biocompatibility in the oral environment, esthetically appealing appearance, ease of handling and processing, and low cost²-⁴. However, it has some disadvantages such as susceptibility to denture fractures, poor wear resistance, insufficient surface hardness, and low flexural strength³,⁴.

Denture fractures are commonly caused by an accident (impact failure) or by small forces imposed during mastication (flexural failure)⁵. For maxillary dentures, most fractures are caused by a combination of fatigue and impact stresses; for mandibular dentures, 80% of fractures are caused by impact stress²-⁴. Flexural failure of denture base materials is the primary mode of clinical failures and stems from the development of microscopic cracks in fatigue stress areas⁷. Key tests to evaluate and compare the mechanical properties of denture base materials are the flexural and the impact strength tests²-⁵.

Many approaches have been used to strengthen PMMA, in a bid to improve its mechanical properties and overcome the abovementioned limitations¹-⁸. Although the addition of different kinds of materials has reinforced polymers, ceromers —to the best of the authors’ knowledge— have not been used as a coating material in dentistry.

Ceramics are among the most biocompatible materials developed for dental restorations. Dental ceramics exhibit many favorable properties, such as biocompatibility, chemical inertness, good esthetics, high compressive strength, diminished plaque accumulation, low thermal conductivity, high abrasion resistance, and excellent color stability⁹.

Ceromers, as coating agents, are used on some plastic materials such as PMMA to improve its wear resistance, hardness, transparency to light, and lifespan under ultraviolet exposure and humid conditions¹⁰. They belong to the category of inorganic-organic hybrid polymeric materials and are used for a vast range of applications in different technological fields¹¹. Hybrid materials are formed by combining organic and inorganic constituents, and these materials can be used as coatings for environmental protection of materials, as scratch-resistant coatings, as a hybrid matrix for fiber-reinforced composites, or as a material for hybrid ceramic body armor.

Ceromer materials contain both hydrocarbon and silicone and exhibit properties that are intermediate between polymers and ceramics¹². Inorganic part of the ceromer molecule is in the ceramic structure, while the organic part is in the polymer structure. The functional group of the ceromer structure binds to the polymer structure, and the other part renders the improved ceramic properties (such as better biocompatibility, hardness, and wear resistance) to the surface¹³. For this reason, ceromers could be used to improve the physical and mechanical properties of PMMA.

Various surface coating techniques have been used for biomedical materials. These processes include physical and chemical vapor deposition¹⁴-¹⁸, ion-assisted deposition (IAD)⁹, plasma immersion ion implantation...
Table 1  Test groups of this study

| Groups | Coating agents | Chemical compounds |
|--------|----------------|-------------------|
| Group 1 | Control group | Non-coated PMMA |
| Group 2 (GT) | GLYMO-TEOS | 3-Glycidoxypropyltrimethoxysilane (GLYMO)-tetraethoxysilane (TEOS) |
| Group 3 (GTT) | GLYMO-TEOS-TiO₂ | 3-Glycidoxypropyltrimethoxysilane (GLYMO)-tetraethoxysilane (TEOS)-TiO₂ |
| Group 4 (GTZ) | GLYMO-TEOS-ZrO₂ | 3-Glycidoxypropyltrimethoxysilane (GLYMO)-tetraethoxysilane (TEOS)-ZrO₂ |
| Group 5 (AT) | A174-TEOS | 3-Methacryloxypropyltrimethoxysilane (A174)-tetraethoxysilane (TEOS) |
Table 2 Compositions of coating solutions

| Chemicals          | Coating Solutions                          | Amounts (g) |
|--------------------|--------------------------------------------|-------------|
|                    | GLYMO-TEOS-TiO₂                            | 0.935       |
|                    | GLYMO-TEOS-ZrO₂                            | 0.935       |
|                    | A174-TEOS GLYMO-TEOS                       | —           |
|                    | GLYMO-TEOS                                 | 0.935       |
| GLYMO              | 0.935                                      |             |
| TEOS               | 0.226                                      |             |
| H₂O                | 0.052                                      |             |
| EGMME              | 7.680                                      |             |
| TiO₂ (10%, w/w)    | 2.313                                      |             |
| ZrO₂ (5%, w/w)     | 2.458                                      |             |
| A174 (in methanol) | —                                          |             |

Coating of PMMA
Using a handmade dip coater at 30 rpm for 10 s, the PMMA surface was coated with one of the four different coating solutions by dip-coating. After a delay of 1 h at room temperature, coated PMMA surfaces were heated to 130°C and polymerized for 2 h at this temperature in an oven (Thermo Scientific Heraeus, Thermo Electron Corp.).

Transverse strength and elastic modulus tests
Before transverse strength test, test specimens were stored in a water bath at 37°C for 50±2 h. Transverse strength and elastic modulus tests were conducted according to ADA Specification No. 12 using a span length of 50 mm and at a crosshead speed of 5.0 mm/min.

All specimens were tested for transverse strength using a three-point loading apparatus until failure in a universal testing machine (LFPlus, Lloyd Instruments, Fareham, UK). Results were recorded using a computer software (Nexygen, Lloyd Instruments, Fareham, UK). Transverse strength (TS) and modulus of elasticity (E) were calculated using the following formulas:

\[
\text{TS} = \frac{3 \times F \times l}{2 \times b \times h^2}
\]

where TS is the stress (MPa), F is the applied load (N) at the highest point of the load-deflection curve, l is the span length (50.0 mm), b (10 mm) is the width of the test specimen, and h (2.5 mm) is the thickness of the test specimen.

\[
\text{E} = \frac{(S \times F)}{(4 \times b \times h^2)}
\]

S is the stiffness (N/m) with S=F/d, and d is the deflection corresponding to load F at a point in the straight line portion of the curve.

Impact strength test
For impact strength test, test specimens were stored in distilled water bath at 37°C for 1 h before the test. Impact strength test was carried out using a Charpy type of impact tester (Pendulum Impact Tester, Coesfeld, Dortmund, Germany). Impact strength (I) was determined using the following formula:

\[
I = \frac{E}{W \times T}
\]

where I (J/m²) is the energy level which breaks the test specimen, W (7.5 mm) is the width of specimen, and T (4 mm) is the thickness.

Scanning electron microscope (SEM) examination
One test specimen from each group was selected for examination under SEM (LEO EVO 40 XVP, Carl Zeiss AG, Oberkochen, Germany). The specimens were sputter-coated with gold using a coater. After coating, SEM microphotographs were taken and visually analyzed.

Statistical analysis
Statistical analyses were performed using Statistical Product for Service Solutions (SPSS) Statistics for Windows, version 11.0 program (SPSS Inc, Chicago, IL, USA). Transverse strength, elastic modulus, and impact strength for each group were reported as means±standard deviation (SD). Normality for continued variables in groups was determined using the Shapiro-Wilk test. The variables did not show normal distribution (p<0.05). Therefore, Kruskal-Wallis and Conover tests were used for the comparison of variables between the studied groups. A value of p<0.05 was considered significant.

RESULTS
Figure 1 is a schematic diagram showing the formation mechanism of GLYMO-TEOS.

Figures 2 and 3 are schematic diagrams showing the formation mechanisms of coating materials which consisted of ZrO₂ and TiO₂ nanoparticles. The surfaces of ZrO₂ and TiO₂ nanoparticles had a substantial number of functional OH groups. Therefore, the alkoxy
Fig. 1 Schematic diagram showing the formation mechanism of the coating material, GLYMO-TEOS.

Fig. 2 Schematic diagram showing the formation mechanism of the coating material which consisted of ZrO$_2$ nanoparticles.

groups of GLYMO and TEOS could react with terminal OH groups on nanoparticles’ surfaces. The polymeric coating material was obtained by further condensation reactions, leading to the formation of inorganic-organic network.

Figure 4 is a schematic diagram showing the formation mechanism of the coating material which consisted of A174 with TEOS. 3-methacryloxypropyltri
methoxysilane (A174) was a silane compound which had a methyl methacrylate group. It was polymerized via the double bond of methacrylate group by radical chain polymerization reaction.

The mean and SD values of impact strength, transverse strength, and elastic modulus for all groups and the results of Kruskal-Wallis test are presented in Table 3.
Table 3  Mean and standard deviation (SD) values of all groups tested for impact strength, transverse strength and elastic modulus and the results of Kruskal-Wallis test

| Control          | 77.16 (4.54)* | 1,141.93 (216.46)* | 11.80 (0.90)* |
| GLYMO-TEOS       | 85.45 (19.16)* | 2,533.63 (420.19) b | 11.02 (3.56) a |
| GLYMO-TEOS-TiO₂  | 96.51 (16.93) b | 2,497.71 (578.17) b | 12.31 (2.03)* |
| GLYMO-TEOS-ZrO₂  | 72.67 (11.54) a | 2,788.46 (460.10) bc | 5.69 (1.05) b |
| A174-TEOS        | 98.15 (9.12) b | 2,105.51 (505.62) bd | 12.97 (2.02)* |
| KW               | 28.46 | 20.57 | 26.45 |
| p value          | 0.0001 | 0.0004 | 0.0001 |

* SD in paranthesis. Superscript letters indicate significant differences p<0.05.

Transverse strength
Post hoc Conover test revealed that coating with GLYMO-TEOS-TiO₂ and A174-TEOS significantly increased the transverse strength compared with the control group (p<0.001).

Elastic modulus
All ceromers caused a statistically significant increase

Fig. 5  SEM photomicrograph of specimen from control group (×500).

Fig. 6  SEM photomicrograph of specimen from GT group (×500).

Fig. 7  SEM photomicrograph of specimen from GTT group (×500).

Fig. 8  SEM photomicrograph of specimen from GTZ group (×500).
in the elastic modulus compared with the control group ($p<0.05$). There was also a significant difference in elastic modulus between GLYMO-TEOS-ZrO$_2$ and A174-TEOS.

**Impact strength**

*Post hoc* Conover test revealed that there were no statistically significant differences in impact strength between the control and coated groups ($p>0.05$), except with GLYMO-TEOS-ZrO$_2$. Compared with the control and the other coated groups, GLYMO-TEOS-ZrO$_2$ significantly decreased the impact strength ($p<0.05$).

**SEM microphotographs of coated PMMA surfaces**

Scanning electron microscopy is a valuable and necessary method to investigate the success of the coating. Therefore, it was carried out in this study to evaluate the coated surfaces. SEM analysis was done at ×500 magnification. Figures 5–9 show the SEM microphotographs of the control and coated groups, revealing that PMMA was successfully coated with the tested ceromers.

**DISCUSSION**

The null hypothesis, which stated that coating with ceromers would not be effective in improvement of the mechanical properties of PMMA, was rejected. This study demonstrated the effect of different coating materials on the flexural properties and impact strength of heat-polymerized denture base polymer. Flexural properties are important criteria in the mechanical strength evaluation of dental materials. Impact strength test was also performed to compare the mechanical properties of denture base materials.

In the present study, it was expected that coating the denture base with ceromers would improve the mechanical properties of PMMA. To test this hypothesis, transverse strength and elastic modulus were examined using a three-point bending method, and impact strength was evaluated using the Charpy method. Statistical analyses revealed significant differences in the mechanical properties. Coating with ceromers increased the elastic modulus of PMMA compared with the control group. All ceromers, except for GLYMO-TEOS-ZrO$_2$, increased the transverse strength of PMMA; however, the increase by GLYMO-TEOS was not statistically significant. GLYMO-TEOS-ZrO$_2$ significantly decreased the impact strength of PMMA.

To overcome the less-than-ideal physical and mechanical properties of PMMA denture base material, various reinforcing methods involving the addition of materials have been proposed, such as metal strengtheners, carbon graphite fiber, aramid fiber, ultra-high molecular weight polyethylene fiber, glass fibers, polystyrene, and urethane dimethacrylate. These reinforcing agents are also less than ideal with their own share of pros and cons, such as difficulty in polishing, bad esthetic quality, and complicated processes. Although reinforcement with glass fibers resulted in good esthetics and chemical bonding to the resin matrix after silane treatment, it has limited efficacy due to non-homogeneous spreading and inadequate impregnation of the fibers with the resin.

In this study, coating with ceromers was a new technique that had never been used for strengthening PMMA denture bases.

Organic-inorganic hybrid materials are eminently suitable to be used for dental coatings. The inorganic part enables certain properties, such as hardness, wear resistance, and biocompatibility, to be improved. The organic part, on the other hand, improves the processing ability of the coatings, such as allowing the coatings to be prepared with low-surface-energy, anti-adhesive properties and therefore limit the tendency to plaque formation. Further, functional groups may contribute toward improving the adhesion of the coating to the dental substrate.

Cytotoxicity and coating material's effect on monomer release are also investigated. Therefore, the effect of coating thickness and the durability of coating materials are ongoing studies.

In general, hybrid coatings are transparent, show good adhesion, and enhance the scratch and abrasion resistance of the coating. For further studies, scratch and wear resistance of coated PMMA, especially for acrylic teeth, should be evaluated.

Hybrid materials processed using the sol-gel technique preserve and combine the most important properties of their constituents, such as high transparency (glass-like), low processing temperatures (polymer-like), sufficient thermal stability (silicone-like), and are easily accessible because of a unique availability of the respective precursors (commercially available metal alkoxides and organo (alkoxy) silanes as well as nanoparticles).

Numerous studies have used the sol-gel method to coat different types of materials. The solution-gelation (sol-gel) method offers a relatively simple
coating method with many applications\textsuperscript{27}. It has been proposed as a suitable procedure to produce protective\textsuperscript{28} and bioactive coatings\textsuperscript{29}. The coatings, obtained using the sol-gel process, are characterized by low thickness, high homogeneity, satisfactory mechanical and chemical stability, good bonding to the substrate, high biocompatibility, and good corrosion resistance\textsuperscript{27}. Thus, these properties render the sol-gel coatings very attractive for use in the dentistry field\textsuperscript{27}.

The sol-gel process also has many advantages, such as increased homogeneity as mixing occurs at the atomic level, ease of fabrication, low processing temperature, reduced sintering temperatures due to small particle size, easy control of coating thickness, the possibility of obtaining both mono- and multi-components which can be multi-layered, and the ability to easily coat complex shapes\textsuperscript{26,27}.

For denture base materials, flexural strength is of prime importance amongst a host of properties such as water sorption, aging, dimensional stability, and biocompatibility\textsuperscript{4}. Two of the coating agents used in this study (GLYMO-TEOS-TiO\textsubscript{2} and A174-TEOS) significantly increased the flexural strength of heat-polymerized PMMA, which is a highly desired property for PMMA.

Ceramics are more rigid materials compared with polymers. By coating PMMA with ceromers, it was expected to gain some of the mechanical properties of ceramic materials. In this study, the elastic moduli of all the coated specimens were significantly increased when compared with the non-coated control group.

In the case of ceromer coating with ZrO\textsubscript{2}, the lackluster mechanical properties were caused by the effect of tetragonal-to-monoclinic phase transformation on the structure of zirconia, such that microcracks formed on the coating surface due to volume expansion\textsuperscript{42,43}. These microcracks absorbed the water used during flexural strength test. Consequently, water sorption reduced the mechanical properties of the material\textsuperscript{42}.

In this study, it was found that coating with ceromers influenced the mechanical properties of PMMA. Coating thickness might also have an effect on the strength of PMMA. Coating thickness used in this study was 1 µm. In future studies, the properties evaluated in this study should be evaluated with different coating thicknesses by virtue of different coating speeds.

Results of this study suggested that coating with GLYMO-TEOS-TiO\textsubscript{2} and A174-TEOS was adequate for improving the mechanical properties of PMMA. These results might have important and beneficial clinical implications. The risk of denture damage is reduced by improving the flexural properties of PMMA, which could be realized by a coating reinforcement instead of fillers.

Denture base resins are used in a humid environment in the oral cavity. When not in use, they are stored in water. Therefore, the effect of water is an important factor. For this reason, it is important to test the solubility and water absorption of coated PMMA. Further studies should be done to investigate the other properties of coated PMMA, including the cytotoxicity of coating materials.

**CONCLUSIONS**

Within the limitations of this study, the following conclusions were made:

1. Coating with ceromers substantially improved the mechanical properties of PMMA.
2. Coating with GLYMO-TEOS-TiO\textsubscript{2} and A174-TEOS had positive effects on all the mechanical properties of PMMA.
3. Coating with GLYMO-TEOS-ZrO\textsubscript{2} decreased the flexural and impact strengths of PMMA, thus increasing the elastic modulus.

**ACKNOWLEDGMENTS**

This study was supported by İnönü University Scientific Investigation Project, Malatya, Turkey.

The authors profusely acknowledge the biostatistical contributions of Prof. Dr. Saim Yoloğlu toward this study.

This study was presented as a poster presentation in FDI 2013 Istanbul-101st Annual World Congress.

**REFERENCES**

1) Vuorinen AM, Dyer SR, Lassila LV, Vallittu PK. Effect of rigid rod polymer filler on mechanical properties of polymethyl methacrylate denture base material. Dent Mater 2008; 24: 708-713.
2) Dikbas I, Gurbuz O, Unalan F, Koksal T. Impact strength of denture polymethyl methacrylate reinforced with different forms of E-glass fibers. Acta Odontol Scand 2013; 71: 727-732.
3) Chaijareenont P, Takahashi H, Nishiyama N, Arksornmuik M. Effect of different amounts of 3-methacryloxypropyltrimethoxysilane on the flexural properties and wear resistance of alumina reinforced PMMA. Dent Mater J 2012; 31: 623-628.
4) Zhang X, Zhang X, Zhu B, Lin K, Chang J. Mechanical and thermal properties of denture PMMA reinforced with silanized aluminum borate whiskers. Dent Mater J 2012; 31: 903-908.
5) Kanie T, Fujii K, Arikawa H, Inoue K. Flexural properties and impact strength of denture base polymer reinforced with woven glass fibers. Dent Mater 2000; 16: 150-158.
6) Kim SH, Watts DC. The effect of reinforcement with woven E-glass fibers on the impact strength of complete dentures fabricated with high-impact acrylic resin. J Prosthet Dent 2004; 91: 274-280.
7) Dogan OM, Bolayir G, Keskin S, Dogan A, Bek B. The evaluation of some flexural properties of a denture base resin reinforced with various aesthetic fibers. J Mater Sci Mater Med 2008; 19: 2343-2349.
8) Karacaer O, Polat TN, Tezvergi1 A, Lassala LVJ, Vallittu PK. The effect of length and concentration of glass fibers on the mechanical properties of an injection-and a compression-molded denture base polymer. J Prosthet Dent 2003; 90: 385-393.
9) Denry I, Holloway JA. Ceramics for dental applications: a review. Materials 2010; 3: 351-368.
10) Cui L, Ranade AN, Matos MA, Pingree LS, Frot TJ, Dubois G, Dauskardt RH. Atmospheric plasma deposited dense silica
coatings on plastics. ACS Appl Mater Interfaces 2012; 4: 6587-6598.

11) Schultzze C, Cordes A, Schmidt W, Sternberg K, Behrend D, Schmitz KP. Hybrid polymers as implant material for medical devices. JFMBE Proc 2009; 25: 164-167.

12) Tiwari A, Hihara LH. Effect of inorganic constituent on nanomechanical and tribological properties of polymer, quasi-ceramic and hybrid coatings. Surf Coat Tech 2012; 206: 4606-4618.

13) Gunogor A, Kayaman-Apohan N, Mert A, Kahraman MV. Preparation and characterization of light curable hybrid coating: Its potential application for dental restorative material. J Polym Res 2008; 15: 389-395.

14) Matsuoka M, Isotani S, Suicasaire W, Zambom LS, Ogata K. Chemical bonding and composition of silicon nitride films prepared by inductively coupled plasma chemical vapor deposition. Surf Coat Tech 2010; 204: 2923-2927.

15) Garcia-Alonso MC, Saldana L, Valles G, Gonzalez-Carrasco JL, Gonzalez-Cabrero J, Martinez ME, Gill-Garay E, Munuera L. In vitro corrosion behavior and osteoblast response of thermally oxidised Ti6Al4V alloy. Biomaterials 2003; 24: 19-26.

16) Lattemann M, Nold E, Ulrich S, Leiiste H, Holleck H. Investigation and characterisation of silicon nitride and silicon carbide thin films. Surf Coat Tech 2003; 174: 365-369.

17) Qian F, Temmel G, Schnupp R, Ryssel H. Thin stoichiometric silicon nitride prepared by r.f. reactive sputtering. Microelectron Reliab 1999; 39: 317-323.

18) Ko SL, Lee CC. Surface characterization and properties of silicon nitride films prepared by ion-assisted deposition. Surf Coat Tech 2010; 204: 3234-3237.

19) Wang RR, Welsch GE, Monteiro O. Silicon nitride coating on titanium to enable titanium-ceramic bonding. J Biomed Mater Res 1999; 46: 262-270.

20) Schullte C, Cordes A, Schmidt W, Sternberg K, Behrend D, Schmitz KP. Hybrid polymers as implant material for medical devices. JFMBE Proc 2009; 25: 164-167.

21) Singh R, Martin M, Dahotre NB. Influence of laser surface modification on corrosion behavior of stainless steel 316L and Ti-6Al-4V in simulated biofluid. Surf Eng 2005; 21: 297-306.

22) Gallardo J, Galliano P, Moreno R, Duran A. Bioactive sol-gel coatings for orthopaedic prosthesis. J Sol-Gel Sci Techn 2000; 19: 107-111.

23) Gallardo J, Galliano P, Moreno R, Duran A. Bioactive sol-gel coatings for orthopaedic prosthesis. J Sol-Gel Sci Techn 2000; 19: 107-111.

24) Olofsson J, Pettersson M, Teuscher N, Heilmann A, Larsson K, Grandfield K, Persson C, Jacobson S, Engqvist H. Fabrication and evaluation of Si6Ny coatings for total joint replacements. J Mater Sci: Mater Med 2012; 23: 1879-1889.

25) Heilmann RB. Thermal spraying of silicon nitride coatings using highly accelerated precursor powder particles. Surf Coat Tech 2010; 205: 943-948.

26) Schottner G. Hybrid sol-gel-derived polymers: Applications of multifunctional materials. Chem Mater 2001; 13: 3422-3435.

27) Medda SK, De G. Inorganic-organic nanocomposite-based hard coatings on plastics using in-situ generated nano-SiO2 bonded with Si=O-Si-PFO hybrid network. Ind Eng Chem Res 2009; 48: 4326-4333.

28) Skoc MS, Macan J, Pozelj E. Modification of polyurethane-coated fabrics by sol-gel thin films. J Appl Polym Sci 2014; 131: 39914-39926.

29) Sanchez C, Julian B, Belleville P, Popall M. Applications of hybrid organic-inorganic nanocomposites. J Mater Chem 2005; 15: 3559-3592.

30) Kim GD, Lee D, Moon JW, Kim JD, Park JA. Synthesis and applications of TEOS/PDMS hybrid material by the sol-gel process. Appl Organometal Chem 1999; 13: 361-372.

31) Wu LXL, Chwa E, Chen Z, Zeng XT. A study towards improving mechanical properties of sol-gel coatings for polycarbonate. Thin Solid Films 2008; 516: 1056-1062.

32) Que W, Sun Z, Lam YL, Chan YC, Kam CH. Effects of titanium content on properties of sol-gel silica-titania films via organically modified silane precursors. J Phys D: Appl Phys 2001; 34: 471-476.

33) American Dental Association (ADA) Council on dental materials and Devices. Revised ADA specification No. 12 for denture base polymers. J Am Dent Assoc 1975; 90: 451-458.

34) Sayilkan F, Asilturk M, Kiraz N, Burunkaya E, Arpac E, Sayilkan H. Photocatalytic antibacterial performance of Sn(+) doped TiO2 thin films on glass substrate. J Hazard Mater 2009; 162: 1309-1316.

35) Asilturk M, Sayilkan F, Erdemoglu S, Akarsu M, Sayilkan H, Erdemoglu M, Arpac E. Characterization of the hydrothermally synthesized nano-TiO2 crystallite and the photocatalytic degradation of Rhodamine B. J Hazard Mater 2006; 131: 399-408.

36) Chevalier J. What future for zirconia as a biomaterial? Biomater 2011; 32: 1043-1058.

37) Devi KB, Singh K, Rajendran N. Sol-gel synthesis and characterisation of nanoporous zirconium titanate coated on 316L SS for biomedical applications. J Sol-Gel Sci Techn 2011; 59: 515-520.