



Thermal and environmental characterization of opaque dental porcelain powder as filler in denture base poly (methyl methacrylate)

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Abstract About 90-95 % of dentures are fabricated from Poly (methyl methacrylate) which is a preferred material for removable complete and partial prostheses. In this study, opaque dental porcelain powder used as ceramic filler was incorporated into the PMMA matrix. The resulting composite was tested for its environmental and thermal qualities for applicability in dental restoration. The diagnosis results of filled and unfilled samples showed that the filler-filled formulations had less water solubility, less absorption and reduced weight loss after 28 days of immersion in SBF at 37°C. The water absorption and solubility values of all filled formulations were below the values specified by the ISO standards for denture base materials. The degradation temperature of the filler-filled PMMA samples was shown to be slightly higher than that of the unfilled samples. The environmental and thermal feasibility tests approved that the prepared composite denture base material is applicable in denture restorations.

Keywords: opaque dental porcelain, Poly (methyl methacrylate), Methyl Methacrylate, Ethylene Glycol Dimethacrylate, denture base materials.

التوصيف الحراري لمسحوق خزف الأسنان غير شفاف كمادة حشو للمواد الأساسية للأسنان

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المخلص يتم تصنيع حوالي 90-95 % من أطقم الأسنان من بولي (ميثيل ميثاكريلات) (PMMA) وهو مادة مفضلة للأطراف الاصطناعية الكاملة والجزئية القابلة للإزالة. في هذه الدراسة، تم دمج مسحوق بورسلان الأسنان المعتم المستخدم في حشو السيراميك في مصفوفة PMMA. تم اختبار المركب الناتج عن خصائصه البيئية والحرارية للتطبيق في ترميم الأسنان. أظهرت نتائج العينات المملوءة وغير المملوءة أن المستحضرات المملوءة بالماء كانت أقل قابلية للذوبان في الماء وأقل امتصاصاً وفقداناً أقل للوزن بعد 28 يوماً من الانغماس في SBF عند 37 درجة مئوية. كانت قيم امتصاص الماء وقابلية الذوبان لجميع المستحضرات المملوءة أقل من القيم المحددة في معايير ISO للمواد الأساسية للأسنان. أظهرت درجة حرارة التحلل لعينات PMMA المملوءة بالماء أعلى قليلاً من درجة حرارة العينات غير المملوءة. وافقت اختبارات الجدوى البيئية والحرارية على أن مادة الأساس المركبة للأسنان المركبة قابلة للتطبيق في عمليات ترميم الأسنان.

الكلمات المفتاحية: مواد الأساس للأسنان، بورسلان الأسنان غير شفاف، بولي (ميثيل ميثاكريلات).

Introduction

In practice, dental materials may perform preventive, restorative or auxiliary roles. Metals, ceramics, polymers, and composites are the main group of materials used in dentistry today [1]. A polymeric matrix with particulate ceramic filler is the most commonly used anterior esthetic restorative material [2]. In addition to adequate physical and mechanical properties, the ideal denture base material should possess several key properties, such as biocompatibility, good aesthetics, high bond strength with available denture teeth, radiopacity, and ease of repair.

Many different materials have been used for denture bases. Historically, materials such as bone, wood, ivory, and vulcanized rubber were utilized. Nowadays, poly (methyl methacrylate) (PMMA) is used. Though new materials such as polystyrene and light-activated urethane dimethacrylate have been developed, PMMA remains the preferred material for removable complete and partial prostheses. PMMA is the most widely used material in prosthetic dentistry. The popularity of PMMA materials is based on its low

cost, relative ease of use, and reliance on simple processing equipment [3]. Although many other materials are utilized as dental prosthetic, none possess traits like PMMA. About 90-95 % of dentures are fabricated from this acrylic polymer [4]. Due to aesthetically pleasing appearance, ease of processing and reparability, PMMA is an excellent denture base material and is more stable in the mouth compared to any of the previously used materials. The popularity of PMMA is associated with its favorable working characteristics, processing ease, accurate fit, stability in oral environment, superior esthetics, and the ability to be used with inexpensive equipment [5]. However, the usage of PMMA when filled with ceramic opaque dental porcelain (ODP) in denture base as reinforcement has never been reported in open literature.

In this paper, a denture base composite material was prepared through the incorporation of ceramic filler ODP to act as reinforcement agent. The environmental and thermal properties of OPD-filled

PMMA composite were investigated and assessed for the feasibility of the prepared composite in dental restoration applications.

Experimental

1. Materials and methods

In this study, the ODP powder which was used as a filler was prepared from raw materials based on the work [6]. The ODP powder was treated with a silane coupling agent (γ -MPS) before incorporated into the solid components (PMMA, BPO).

Three different ratios (i.e. 5%, 10% and 15% by weight) of treated and untreated fillers were added into the PMMA matrix with high molecular weight (i.e. 996,000 GPC Aldrich U.S.A) plus 0.5 % BPO (Merck Chemical, Germany). The composite was then mixed using the ball milling technique for 1h. The mixture was added into MMA monomer (fluka, UK) and stabilized with 0.0025% hydroquinone plus cross linking agent (10%) EGDMA (Aldrich USA).

The mixing ratio of powder to liquid (P/L) was 2.5:1 which is according to dental laboratory usage. Environmental characterization of the treated and untreated samples was carried out to test the water absorption properties using water immersion test according to the ASTM D570-98 standard. Tests for Simulated Body Fluid absorption and solubility properties were carried out according to the ISO 1567-2000 standard (SBF) while the thermal properties were examined using thermogravimetric Analysis (TGA). The procedures of this study are consistent with the prescribed standard method for preparation of a conventional denture base in the dental laboratory [7].

2. Sample Characterization

2.1 Absorption and solubility analysis

Absorption and solubility in liquid media affect the mechanical properties of composite materials. PMMA molecular polarity facilitates the water absorption property. When water diffuses into the polymer matrix, it causes expansion of the polymerization mass and thus; weakening the composite's mechanical properties [1, 8]. A water absorption test was carried out according to the ASTM D570-98 standard, while an SBF absorption test and SBF solubility test were carried out according to the ISO 1567-2000 standard. In all tests, the specimens were cut to 0.5-0.6 g using band saw, and polished using SiC paper p280 and p1200 respectively, to improve the surface finish and to remove cutting marks. Five specimens were prepared for each material formulation (5%, 10% and 15% ODP, respectively). The specimens were dried in a vacuum oven at $37 \pm 2^\circ\text{C}$ for 24 hr and kept in a desiccator containing silica gel for 24 hrs prior to immersion in distilled water or in SBF (B-Braun Medical Industries, Penang, Malaysia). The specimens were then weighed using an analytical balance of reading 0.0001 g then immersed in distilled water (for water absorption test) or in SBF at 37°C in a water bath (for SBF absorption test) at room temperature, and weighed after 1, 7, 14, 21, and 28 days, respectively. The change in weight for

all tests of absorption and solubility was calculated by the equation 1:

$$\text{Change in weight} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

Where; W_0 and W_1 are weight of sample before and after immersion.

2.2 Thermal analysis

Since polymers have higher thermal coefficients than most rigid fillers, filler incorporation into polymer matrix may cause changes in the thermal and mechanical properties of the composite (e.g. induce thermal stress, weight loss/gain, microcracks, fabrication failure, etc.). So, heating a polymer sample allows observation of the changes in physical properties associated with changes in the degree of packing and chain-chain interaction [9]. For the thermal stability test, samples from all parts of a dumbbell specimen were taken, collected and analyzed using TGA to confirm the filler content as well as to determine the dispersion of fillers throughout the dumb bell. The experiment was carried out with a Perkin – Elmer Pyris 6 TGA analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ from 50°C to 550°C in the presence of nitrogen air flow of 50 ml/min. The sample of the test material was placed in a high alumina cup suspended from an analytical balance located outside the furnace chamber. The balance was zeroed, and the sample cup was heated. The temperature was raised gradually and the weight against temperature was plotted in order to get thermogravimetric curves, i.e. thermograms. The balance sent the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The test results were a graph of the TGA signal (actual weight loss or gain converted to percent weight loss) on the y-axis plotted versus the reference sample temperature in $^\circ\text{C}$ on the x-axis. The sample's weight loss as the temperature increased provides insights to degradation rate and filler content.

3. Results and discussion

3.1 Water absorption

Exposure of restorative materials to an aqueous environment lowers the values of their mechanical properties, e.g. strength, hardness and elastic modulus [10] and dimensional stability of the resins. Therefore, water absorption should be suppressed in the dental composite resins. **Figure 1** illustrates the water absorption values of various denture base formulations immersed in water at room temperature. A general look at the figure implies that in all samples the water uptake increases steadily with time and ultimately reaches to a constant value after 28 days of immersion.

Table 1 shows the water absorption measurement values of opaque dental porcelain filled-PMMA composite, conventional denture base material and unfilled PMMA compared to ISO 1567-2000 after 28 days of immersion. It can be seen that the

amount of water absorption of filled-PMMA formulations are lower than that of the PMMA matrix. It is also noted that the amount of water absorption increases steadily with time until the saturation state is reached after 28 days of immersion. On the other hand, the amount of absorption in the 15 wt % formulation is the lowest among all formulations. These findings were in accordance with the results of Elshereksi [11] who used BaTiO₃ as filler material in PMMA. He found that the formulations 15 wt % and 20 wt% had the lowest water absorption compared to the formulations of 5 and 10 wt%. The increase in weight can be associated to the occurrence of two main processes in the sample: monomer extraction and water diffusion into the polymer. Residual MMA is composed of extractable and non-extractable parts. The extractable part is associated with the surface of the material, which have lower temperatures than the internal part upon polymerization. The non-extractable parts refer to the molecules trapped in the long polymer chains. Therefore, the actual change in weight of the specimens was a combination of weight increase due to water uptake and weight loss due to leaching of the monomer [12]. From **Table 1**, the water absorption of all filler formulations is below the value specified by the ISO 1567-2000 standards for denture base materials.

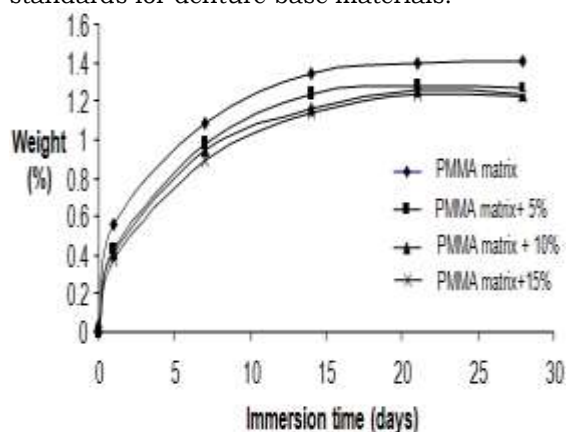


Fig. 1: Water Absorption Values of Opaque Dental Porcelain-Filled PMMA Composite Compared to that of Unfilled PMMA after 28 Days of Immersion at Room Temperature

Table 1: Water Absorption Values of Opaque Dental Porcelain-Filled PMMA Composite Compared to Unfilled PMMA after 28 Days Immersion in Water at Room Temperature

Formulation	Amount of water absorption (%)	Corresponding of water absorption ($\mu\text{g}/\text{mm}^2$)
PMMA matrix	1.41	22.67
PMMA+5 wt % Filler	1.27	20.42
PMMA+10 wt % Filler	1.24	19.93
PMMA+15 wt % Filler	1.22	19.61

ISO standard(1567-2000) value: max weight increase percentage: 1.99%, corresponding to 32 $\mu\text{g}/\text{mm}^2$

3.2 Absorption of Simulated Body Fluid (SBF)

Figure 2 illustrates the values of SBF absorption by opaque dental porcelain-filled PMMA composite and the neat PMMA after 28 days of immersion in

SBF at 37°C in comparison to the ISO 1567-2000 standard. The curves show an increasing trend, similar to water absorption. An initial increase in SBF amount is observed to happen steadily up to 14 days. After that, there was no significant change in weight (up to 28 days).

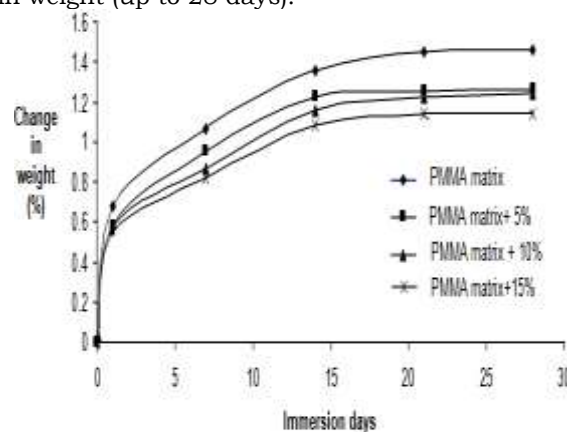


Fig. 2: SBF Absorption Curves of Opaque Dental Porcelain-Filled PMMA Composite Compared to that of the Unfilled PMMA after 28 Days Immersion at 37°C

Table 2 shows the SBF absorption values of opaque dental porcelain filled PMMA composite, and unfilled PMMA after 28 days of immersion in SBF at 37°C compared with the ISO standards. The values of SBF absorption for all formulations were well below the values specified by ISO 1567-2000 standards. In addition, it is noted that the SBF values of the filled PMMA samples were lower than the value of the neat PMMA matrix. This can be attributed to the presence of the silane coupling agent which reduced the hydrophilicity of the ceramic filler. According to Santos [13], the hydrophobic nature of the treated ceramic filler surface will inhibit the ability of the composites to absorb water. When the polymer resin composite was soaked in an aqueous environment, two processes occurred. Firstly, a rapid elution of uncured monomer took place, which appears to have been completed within several days. Simultaneously, SBF was absorbed by the composite, predominantly by diffusion into the polymer matrix [14].

Table 2: SBF Absorption Values of PMMA Composites Compared to that of the Unfilled PMMA after 28 Days in SBF at 37°C

Formulation	Weight increase by (%)	Mass weight increase by ($\mu\text{g}/\text{mm}^2$)
PMMA matrix	1.46	23.1
PMMA+5 wt % Filler	1.26	20.26
PMMA+10 wt % Filler	1.24	19.93
PMMA+15 wt % Filler	1.14	18.33

3.3 Solubility in Simulated Body Fluid (SBF)

Table 3 summarizes the solubility values of ODP-filled PMMA composite compared to that of the unfilled PMMA after 28 days of immersion in SBF at 37°C. It is evident from the table that the solubility values are below the ISO specifications. After the specimens were stored in simulated body fluid, their weights were found to decrease.

However, the fact that the PMMA remained insoluble in water implies that the initial weight decrease cannot be attributed to the dissociation of resin in water [15]. The actual change in weight of the specimens was a combination of weight increase due to water uptake and weight loss due to leaching of the monomer [16]. It is noted that the lower solubility of the filled formulations was below that of the unfilled PMMA matrix. The reduced weight loss in the treated filled samples is associated with the presence of a silane coupling agent on the filler's surfaces which generated a hydrophobic surface [16].

Table 3: Solubility Values of PMMA Composite Compared to that of the PMMA Matrix after 28 Days Immersion in SBF at 37°C.

Formulation	Weight loss (%)	Mass Weight loss ($\mu\text{g}/\text{mm}^2$)
PMMA matrix	1.46	23.1
PMMA+5 wt % Filler	1.26	20.26
PMMA+10 wt % Filler	1.24	19.93
PMMA+15 wt % Filler	1.14	18.33

ISO (1567-2000) Standard Value: Max Weight Loss Percentage: 0.99%, Max Weight Increase: 1.6 $\mu\text{g}/\text{mm}^2$

3.4 Thermogravimetric Analysis (TGA)

Figure 3 shows the results of TGA scan for all formulations of denture base material, filled and unfilled. The thermograms show little weight loss up to a temperature of 250-300°C. After this temperature, a sharp decrease in weight is observed and at temperature 425-445°C, almost complete weight loss is observed, leaving only the filler residue. It is evident that there are differences in the thermal degradation patterns for different formulations. It was noted that the degradation temperature of the opaque dental porcelain-filled samples is slightly higher than that of the PMMA unfilled samples. The unfilled PMMA sample displayed no residual material formation at temperatures of up to 440°C. This behavior indicates the occurrence of random chain scission that the PMMA polymer undergoes as degradation progresses [17].

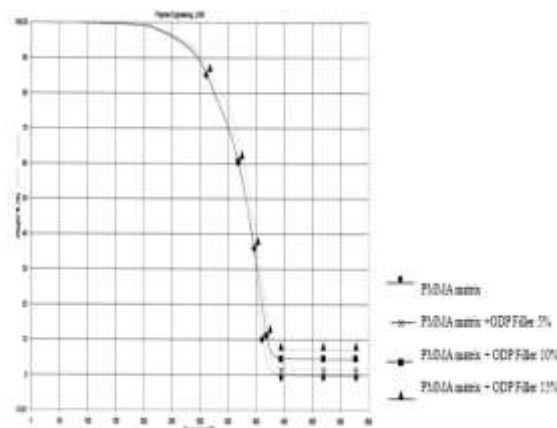


Fig. 3: TGA Curves Illustrating the Thermal Degradation Temperature of the PMMA Composites Compared to PMMA Matrix

All filled-PMMA samples present similar thermal pattern although some slight differences are seen in the thermal degradation temperatures of 15 and

5 wt% formulations (15 wt% have slightly higher degradation temperature than that of 5 wt% sample). This indicates that the 15 wt% filled content is more thermally stable than that of the 5 wt% sample. This finding was in accordance with the findings of Elsherkesi [11] who reported that the formulation 20 wt% of BaTiO₃ filled- PMMA was more thermally stable than that of the 5 wt% sample. From the TGA curves, the degradation ratio increased more rapidly above 300°C. Hu and Chen [18] stated that in the polymer chain, vinyl end groups are less stable with a weaker bonding chain, and unzip the polymer chains radically through a chain transfer process to start degradation at about 220 °C. Consequently, as temperature increases above 300 °C, the random scission constitutes the mechanism of degradation and the de-polymerization rate increases due to main chain scission.

4. Conclusion

The environmental characterization of water solubility and adsorption qualities revealed that the formulations of the prepared composite samples of ODP filler-filled PMMA have lower responses than that of the untreated samples. The filler treated samples also showed reduced weight loss. This was attributed to the effect of the silane coupling agent that suppresses the water hydrophilicity of the filler by producing a hydrophobic surface on the filler particles. The water absorption and solubility values of all filled formulations were below the values specified by the ISO 1567-2000 standards for denture base materials. The degradation temperature of the ODP filler-filled PMMA samples were shown to be slightly higher than that of the unfilled samples. Samples treated with 15 wt% ODP had a higher degradation temperature than that of the 5 wt% sample, indicating that the 15 wt% filled sample has higher thermal stability than that of the 5 wt% sample. The thermal and environmental properties of the prepared samples that were dignosed in this study are expected to enhance the clinical-mechanical properties of the denture base material for restorative applications.

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