Influence of Al$_2$O$_3$/Y-TSZ mixture as filler loading on the radiopacity of PMMA denture base composites

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Abstract

The radiopacity of alumina/yttrium stabilizer zirconia (Al$_2$O$_3$/Y-TSZ) particles with nitrile butadiene rubber (NBR) dispersed in PMMA denture base material has been investigated. PMMA matrix without filler was prepared from PMMA powder with 0.5% benzoyl peroxide (PBO) as the control material. The similar PMMA matrix was mixed with Al$_2$O$_3$/Y-TSZ (1:1) together with NBR particles as the reinforcement. The amount of NBR was fixed at 7.5 wt %, however, Al$_2$O$_3$/Y-TSZ varied from 1 to 10 wt %, respectively. Samples with 4 mm thickness for each composition were irradiated using 60 KV, 10 mA, 0.4 s to examine their radiopacity. This radiopacity was compared to radiopacity of aluminum plate which having the same thickness. The result shows that the radiopacity (i.e. the lower optical density the higher radiopacity) of reinforced PMMA matrix slightly increased from 1.40 to 1.05, respectively, with the increased of filler loading compared to unreinforced PMMA matrix.

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1. Introduction

The denture base should be ideally radiopaque and capable to be detected using normal diagnostic radiographic techniques and measurement of the ability of electromagnetism to pass through a particular material. Radiopacity is an essential property for all restorative materials. The patient may ingest (swallow) these fragments of denture fracture. Therefore, pure denture base is necessary to be radiopaque for easy radiological detection. In a previous study, by a review about 123 cases of swallowed or aspirated dentures or fragments of denture base demonstrated that need for radiopaque for detection these particles, the difficulties and time involved in locating these fragments of the denture bases. Incorporation of opaque filler such as metal or ceramic could be the way out. There were attempts to increase radiopacity by adding barium sulphate by ratio 8% to acrylic resin and however, this did not yield sufficient levels of radiopacity. Increasing the barium sulphate content by ratio 20% gives sufficient radiopacity but unfortunately it has a deleterious effect on the mechanical properties of the resin.

The basic problems of the denture based to be easily radiologically detected and radiolucent because of C, O and H atoms are poor X-ray absorbers. The patient occasionally swallows dentures and may even inhale fragment of denture if involved in a violent accident such as car crash. Therefore, radiological detection fragment of denture is used to help the treatment of the patient. Early method for detection was through the incorporation of heavy-metal salts as physical mixtures with the polymers. Another approach is through the incorporation of glass containing such as barium, aluminum, strontium, zinc and zirconia, respectively, to produce composites that are radiopaque (impenetrable by X-rays), thus enhancing their visibility on a
radiographic film. This is important for diagnostic purposes and radiographs that can be used to differentiate between various specimens based on their radiopacities. Radiopacity of dental resin composites usually resulted from the incorporation of elements of relatively high atomic numbers such as Ba, Zr, Sr, V and La into the resin matrix.

Many attempts were tried to achieve higher radiopacity values for PMMA as denture base material as well as bone cement. Dental materials were developed using heat-curing PMMA, prepared by mixing liquid and powder components. The liquid component contains, MMA as monomer, an inhibitor for preventing the premature polymerization of the monomer and promoter of initiator decomposition. The powder component contains, PMMA as polymer, a mineral powder such as barium sulfate (BaSO₄) or zirconium dioxide (ZrO₂) acting as radiopacity and free radical initiator (typically benzoyl peroxide, BPO). Abboud et al. investigated reinforcement using Al₂O₃ particles treated by γ-MPS. The experiments showed that 4% of Al₂O₃ in cement is sufficient for providing a good opacity for X-rays. A few of denture base materials contain heavy metal compounds or elements such as barium or radiopaque glass filler added to improve the radiopacity. It is necessary to add up to 20% by weight of these compounds to give sufficient radiopacity and this result in a reduction in the strength of the material and change in the appearance of the denture. The weight fraction of the filler and matrix in resin composites influenced the scattering and diffraction of the X-ray interaction. Most of the prostheses investigated are radiopaque though the removable prostheses most likely to be radiolucent. For this reason, the removable prostheses, full acrylic denture were not visible while the upper partial acrylic denture was moderately visible. For example, the PMMA denture base easily broken during accidents or when the patient applies high mastication force and also the patient may even accidentally ingest (swallow) these particles. Besides that, it is also radiolucent and cannot be detected by soft tissues.

Therefore, the purpose of this study is to prepare heat curing PMMA denture base composites containing micron-size ceramic fillers particles (Al₂O₃/Y-TSZ) together with 7.5 wt% NBR (as an impact modifier) in PMMA composite and investigate their radiopacity compared to aluminum plate (reference standard), commercial PMMA and PMMA matrix. In dental application, reinforcement by Al₂O₃/Y-TSZ as filler loading is possible provide to this property in PMMA denture base.

2. Materials and methods

The materials that used in this research are PMMA powder (Mw, 996.000 g/mol; Sigma Aldrich USA), benzoyl peroxide (Merck chemical, Darmstadt, Germany), and MMA monomer “Fluka, UK” with EGDMA (Sigma-Aldrich, USA), 99% purity Al₂O₃ particles (SulzerMetco, Westbury, NJ, 4.4 μm average particle size and density 2.70 g/cm³), Y-TSZ particles (containing 6.38 of Y₂O₃ stabilizer, GoodFellow Cambridge Limited, USA, 1.05 μm, average particle size and density 5.90 g/cm³), and NBR particles (Genzo Scientific Ent., Malaysia, less than 150 μm and density 0.98 g/cm³).

The PMMA denture base material was prepared using powder components mixed with liquid component. The powder components were comprised of PMMA powder, NBR as impact modifier particles, Al₂O₃/Y-TSZ powder was added each other by 1:1 ratios as mixture filler and then, it was mixed with 7.5 wt % NBR particles using 1, 3, 5, 7 and 10 wt %, respectively. Each mixture was mixed for 30 min by using internal mixer (599957-K model, MS Instruments, Malaysia). The rotor speed was 50 rpm and heated at 65 °C. The mixing chamber was cleaned before next mixing process to avoid contamination. The liquid was comprised of 10 % EGDMA as cross-linking agent and 90% MMA as an activator containing 0.025 % hydroquinone as inhibitor (liquid component).

Each of the powder mixture components were mixed with liquid component by hand mixing, respectively. The mixing of powder mixture to liquid medium (P/L) ratio was set at 2.5:1, according to standard dental laboratory usage. The composite reached the dough stage (working stage) for easy forming of the paste around 15 min, the mixture was packed into the specific mold. After that, the mold was pressed under 14 MPa using a hydraulic press (Mestra 48150 Sondika -Bilbao, Spain) maintained under pressure for 30 min at room temperature. The curing process is carried out by placing the mold in a water bath. The temperature of water bath was kept at 78 °C for 90 min to complete the heat polymerization. The mold was removed from the water bath and then left to cool slowly to room temperature. The samples were removed from the mold, then, trimmed and polished by using emery paper 240. This procedure is in accordance to ISO 1567:2001 dentistry-denture base polymer standard method for preparing a conventional denture base in a dental laboratory.

Radiopacity test was assessed according to ISO 4049–2009 standard specifications. The experimental procedure was carried out according to the following produces; the specimens, the aluminum plate and the film were irradiated with X-ray at 60 kV, 10 mA and the exposure time of 0.4 s using an X-ray machine (Toshiba KXO-15R, Japan). The aluminum plate had compositions of, at least 98% of aluminum, 0.1% of copper and 0.1% of iron present in plate. While, dimensions of aluminum plate, the length 50 mm × 20 mm width, having a thickness range from 0.5 mm to 5.0 mm. The film density of each formulation’s image was measured by optical density (OD) using a densitometer machine (RMI, USA). The OD of the test samples were then expressed in terms of equivalent aluminum thickness (mm) by reference to the calibration curve for the OD of the aluminum step-wedge (Fig.1).
Statistical analyses of data

The calculated values of results of tests were performed with statistical analyses (Statistical Package for the Social Sciences (SPSS) statistics version 20) of variance one-way (ANOVA) followed by Tukey’s post-hoc. The results of the tests are considered significant when \( P \leq 0.05 \).

4. Results and discussion

Fig. 2 shows the radiopacity test for the PMMA denture base the specimens compared to aluminum specimen represent the standard radiopaque properties (according to ISO 4049 –2009 standard specifications) in which it is white in the image. The formulations of different additions of \( \text{Al}_2\text{O}_3/\text{Y-TSZ} \) composite of 1, 3, 5, 7 and 10 wt % show slightly visible in ratios 7 and 10 wt % than remain the formulations compared to PMMA matrix, and commercial PMMA as shown in Table 1 and Fig. 2. The result showed higher filler loading give higher radiopacity property. The PMMA matrix itself (without filler) is not radiopaque, making it more difficult for radiographic detection of these particles of denture fracture when the patient may ingest (swallow) these particles. Therefore, the increment of filler ratios into PMMA material will improve in radiopacity of denture base material but this will lead to undesirable effects such as reductions in the mechanical properties.

Fig. 3 shows a comparison of optical density (OD is the reverse value of radiopacity) of PMMA matrix, and reinforced PMMA matrix compared to that aluminum plate. The aluminum plate is highly reflective of the incident radiation; hence, it is of low OD. Table 1 shows that the PMMA matrix show the lowest radiopacity compared with reinforced PMMA incorporate with various percentages of filler content. When the matrix reinforced with 10 wt % of \( \text{Al}_2\text{O}_3/\text{Y-TSZ} \) mixture the radiopacity is 25% (it observed in OD data as shown in Fig. 3) higher than the PMMA matrix (\( P < 0.05 \)). This radiopacity improvement is suitable for denture base (prosthodontics) detection by X-ray technique patient treatment 13. This basically mainly contributed by \( \text{Y-TSZ} \) that shows the highest radiopacity 12 and \( \text{Al}_2\text{O}_3 \) also show a good radiopacity of addition into PMMA denture base 7.
Furthermore, the addition of Al$_2$O$_3$/Y-TSZ as filler loading into PMMA denture base material is slightly improved in radiopacity (the lower optical density the higher radiopacity) of PMMA denture base from 1.40 to 1.05, respectively. This is attributed to high amount (10 wt%) of filler content added in PMMA composite. Filler type and amount of radiopaque fillers may influence the radiopacity of resin-based materials. The higher filler fraction contributed to better radiopacity of the composite. Similar observation that reported by Ihab and Moudhafar by addition of ZrO$_2$ particles in the acrylic denture base and the result was increased in radiopacity (decreased in radiographic density) compared to acrylic denture base without filler. This is due to presence of radiopaque ZrO$_2$ powder in the polymer matrix which absorbs more radiation than polymer matrix and appears more radiopaque and also due to high atomic number of Zr compared to the chemical constituent of acrylic which low atomic number.

5. Conclusion

The radiopacity property is important in denture base (removable prosthodontics). It can improve up to 25% OD when added 7.5% NBR with together 1% Al$_2$O$_3$/1% Y-TSZ mixture compared to PMMA matrix. Therefore, the reinforced PMMA with
Al₂O₃/Y-TSZ composite considered suitable for the dental restorations in dentistry field.

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References