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Mechanical Properties of PMMA Denture Base Reinforced by Nitrile Rubber Particles with Al_2O_3/YSZ Fillers

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Abstract

The aim of this research study is to investigate the effect of filler loading of alumina/yttrium stabilizer zirconia (Al_2O_3/YSZ) filler with nitrile-butadiene rubber (NBR) particles filled PMMA denture base material on the mechanical properties. The PMMA matrix (control group) was prepared 0.5% benzoyl peroxide (BPO) with PMMA powder as initiator. Al_2O_3/YSZ ceramic powders by ratio 50/50 using 1,3,5,7 and 10 wt% as filler loading and then, mixed with10 wt% NBR particles, respectively, into PMMA matrix using the internal mixture as powder mixture (powder component). The liquid component consists of 90% of methyl methacrylate (MMA) and 10% ethylene glycol dimethacryate (EGDMA as the crosslinking agent). The mechanical properties of NBR/treated ceramic fillers in PMMA composites were tested using impact strength (IS) and fracture toughness (K_{IC}). The morphology of fracture surface of specimens was characterized using field emission scanning electron microscopy (FESEM). The IS and K_{IC} values increased to 10.25 KJ/m^2 and 2.58 MPa.m$^{1/2}$ by 5% of loading filler compared to control group 5.27 KJ/m^2 and 1.6 MPa.m$^{1/2}$, respectively. Statistically, shows that the IS and K_{IC} for PMMA reinforced by NBR and Al_2O_3/YSZ is significantly improved ($P < 0.05$). Therefore, this reinforced PMMA denture base is suitable to be used as prosthodontics applications.

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Keywords: PMMA denture base; Nitrile rubber particles; Al_2O_3/YSZ filler; Mechanical properties

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1. Introduction

The most popular material used in removable prosthetic base material is poly (methyl methacrylate) (PMMA) since its introduction in 1937, it remains most popular of all the polymeric denture base materials. It commonly consists of especially poly (methyl methacrylate) (PMMA) as powder form and methyl methacrylate (MMA) as liquid form of heat cured polymerization technique [1]. The popularity of PMMA depends on its easy laboratory and clinical manipulation, ease in finishing and polishing, inexpensive equipment's, stable in the oral environment, and good aesthetic appearance. Ideally, a denture base should have sufficiently high impact strength to prevent breakage on accidental dropping, but not at the expense of the other properties [2].

One of the main problems associated with PMMA is the mechanical strength [3]. The PMMA material is typically low in strength, as well as brittle on impact, and fairly resistant to fatigue. The geometry of the denture base is complex and stresses can be concentrated in frenum notches, cracks might occur in the denture base. Problems in the field of prosthodontics and are mainly represented by two patterns; 1) biting and mastication forces, 2) high-impact forces may occur as a result of accident dropping lead to denture fracture [4]. Impact failure occurs as a result of a fatigue fracture of denture bases is a common clinical problem due to its brittleness [5]. In a study made by Darbar et al. [5], it was reported that 33% of the repairs carried out were due to debonded/detached teeth and 29% were repairs to midline fractures more commonly seen in upper complete dentures. Studies have shown that 68% of PMMA dentures break within a few years of fabrication [6]. As the fracture resistance of a denture base resin is important, many approaches have been used to strengthen PMMA resin dentures. Basically, adequate impact strength and fracture toughness are the most important requirement for denture-based PMMA resins [7, 8]. However, the material possesses poor mechanical strength when used alone and its primary problem [9, 10]. PMMA denture base materials have poor strength, including low impact strength and low fatigue resistance [11].

To solve these problems and to enhance the mechanical properties of PMMA denture base, the addition of fillers and rubber particles in the PMMA resin matrix have been suggested. Other similar result is found in work done [12] using HA. However, Asar et al. [13] found that by using ZrO_2, Al_2O_3, and TiO_2 resulted in the fracture toughness and impact strength is slightly increased. Other researchers were using mixture of ZrO_2/TiO_2 [13], and ZrO_2/Al_2O_3 [14] which also produced similar results. Recently, incorporation of nanotube technology such as [15] using carbon nanotube, result was increased in the impact strength and Yu et al. [16] used ZrO_2 nanotube, the result was higher fracture toughness. In 1930 the synthetic resins started to replace vulcanite rubber as denture base material [9]. PMMA denture base was modified by butadiene-styrene copolymer rubber and improving the impact strength [17]. However, another type of rubber, nitrile butadiene rubber (NBR) has never been reported being used as PMMA denture base reinforcement. NBR has various advantages that may improve the properties of the PMMA denture base such as no allergic reaction to contact oral tissue of prostheses- non-toxic [18], besides act as impact modifier to increase the impact strength. The purpose of this present study was to investigate the effect of nitrile rubber (NBR) as particles with treated Al_2O_3/YSZ mixture filler of heat-polymerized PMMA denture base on the impact strength and fracture toughness. The nitrile butadiene rubber acted as impact modifier whiles the ceramic fillers important for the toughening mechanisms and is most effective for reinforcing PMMA denture base. To date, no report has been done in previous studies.

Nomenclature

Al_2O_3	Alumina Oxide
BPO	Benzoyl peroxide
CVN	Charpy V-notch impact test
EGDMA	Ethylene glycol dimethacryate
IS	Impact strength
K_{IC}	Fracture toughness of the critical intensity factor
MMA	Methyl methacrylate
NBR	Acrylonitrile-butadiene rubber
PMMA	Poly (methyl methacrylate)
YSZ	Yttrium stabilizer zirconia
Gamma-γ-MPS	3-methacryloxy propyl trimethoxysilane

2. Experimental detail

2.1 Materials

The raw 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 (Fluke UK). (EGDMA) (Sigma-Aldrich, USA), 99% purity Al_2O_3 particles (SulzerMetco, Westbury, NJ) (4.4 μm average particle size and density 2.70 g/cm^3), 90% purity YSZ particles (containing 6.38 of Y_2O_3 stabilizer) (GoodFellow Cambridge Limited, USA) (1.05 μm, average particle size and density 5.90 g/cm^3). The silane coupling agent 3-trimethoxysilyl propylmethacrylate (γ-MPS) also known a {3-(methacryloxy) propyl trimethoxysilane} (gamma-MPS), was supplied by Sigma-Aldrich and NBR particles (Genzo Scientific Ent., Malaysia) (less than 150 μm and density 0.98 g/cm^3).

2.2 *Preparation of nitrile butadiene rubber particles*

NBR gloves were passed through a two-roll rubber mixing mill (Shangha Rubber Machine, China) for 5 min at room temperature to obtain strips of nitrile rubber. These strips were ground to obtain in the particles form by table type pulverizing machine (Rong Tsong Precision Tech. Co. Ltd., Taiwan). The particles were sieved to pass through 150 μm. The particles size and distribution were analysed by particle size analyzer (Mastersizer Instrument, UK).

2.3 *Samples preparation of the PMMA denture base composites*

The PMMA denture base material was prepared using powder components mixed with liquid medium. The powder components were comprised of PMMA powder, Al_2O_3/YSZ ceramic powder as filler loading using 1,3,5,7 and 10 wt%, respectively, mixed with10 wt% NBR particles as impact modifier particles. There are 5 different mixtures used in this study as shown in Table 1. 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. Each of the powder mixture components were mixed with liquid medium by hand mixing, respectively. Chow et al. [12] reported that the mixing of powder mixture to liquid medium P/L ratio was set at 2.5: 1, according to standard dental laboratory usage as described [19]. The composite reached the dough 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 and the temperature 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 [19].

Table 1. The powder mixture components ratios; NBR fixed at 10 wt% , 50%Al_2O_3/50%YSZ particles as filler loading in PMMA denture base.

Material	PMMA	BPO	Rubber particles	Ceramic fillers
PMMA matrix	99.5	0.5	-	-
PMMA-10% NBR-1% ceramic filler	88.5	0.5	10	1
PMMA-10% NBR-3% ceramic filler	86.5	0.5	10	3
PMMA-10% NBR-5% ceramic filler	84.5	0.5	10	5
PMMA-10% NBR-7% ceramic filler	82.5	0.5	10	7
PMMA-10% NBR-10% ceramic filler	79.5	0.5	10	10

2.4 Mechanical tests

Charpy V-notch impact test (CVN), was measured using a Zwick pendulum impact tester. The dimensions of samples were 80 mm x 10 mm x 4 mm, the width under notch bn 9.75 mm as required by ISO 179-A1:2005. The specimens were prepared on the V-notch length 0.25 mm radius and the angle notch sensitivity was (rn) 45° by using notched bar impact strength and span support 62 mm. The result was recorded using the following Eq 1. While, the fracture toughness test was determined using the single edge span notch bending test (SEN-B) and the specimens were prepared according to ISO 13586:2000. The dimensions of the specimens were fixed as follows: 100 mm x 20 mm x 4 mm, having notch length 4 mm and the support span length 64 mm [14]. A crack was made on the specimens by tapping a new razor blade placed at the notch on the specimen. The specimens were tested using Instron (3366, 10 KN) at a crosshead speed of 1.00 mm/min. In this case, the fracture toughness of the critical intensity factor (K_{IC}) values was calculated using Eq 2 [20. 21]:

$$(IS) = \frac{E}{b_n t}\, x\, 10^3 \tag{1}$$

$$K_{IC} = \frac{P\frac{S}{2}}{t\frac{W^2}{3}}\left[1.93\left(\frac{a}{w}\right)^{1/2} - 3.07\left(\frac{a}{w}\right)^{3/2} + 14.53\left(\frac{a}{w}\right)^{5/2} - 25.11\left(\frac{a}{w}\right)^{7/2} + 25.80\left(\frac{a}{w}\right)^{9/2}\right] a^{\frac{1}{2}} \tag{2}$$

Where E is value of energy that absorption it the specimen when the impact resistance (J); bn is the specimen width (mm); P is load at peak (N); S is the span length (mm); a is the notch length (mm); t is the specimen thickness (mm); and w is the specimen width (mm).

3. Statistical analyses of data

Statistical analysis of the results for each test were conducted using one-way analysis of variance (ANOVA) followed by Tukey's post-hoc, with significance denoted at $P \leq 0.05$.

4. Results and Discussion

The effects of these PMMA matrix reinforcements on their mechanical properties are shown in Fig 1(A and B). The notice in Fig 1(A), the impact strength (IS) or the PMMA matrix reinforced by 10 wt% NBR particles with 50%Al_2O_3/50%YSZ mixture as filler loading treated by silane a coupling agent. The IS value for unreinforced PMMA denture base reduced compared to reinforced PMMA matrix by 10% nitrile butadiene rubber (NBR) with Al_2O_3/YSZ filler loading (1, 3, 5, 7 and 10%). Brittle behaviour indicting also decrease in impact properties may be attributed to problems at interface between the filler and PMMA matrix [9, 22]. Brittle fracture is a distinct property of materials with reduces in strength resistance value into force load [23]. Impact energy is to measure the resistance to failure of a material to a suddenly applied force and the energy absorbed prior to fracture. Generally, brittle materials have lower impact strength [22]. Reinforced PMMA matrix gradually increase with increasing the filler content up to 5 wt% ceramic filler compared to PMMA matrix and this is due to the presence NBR particles and distribution in the PMMA composites. The addition of 7 and 10 wt% filler content was decreased compared to 1, 3 and 5 wt% filler loading in PMMA matrix. This is due to the filler has relatively low compatibility with the matrix and lowered the capability of matrix to distribute the impact energy applied [24]. Statistically, the IS values were significantly increased ($P < 0.05$). Similar observation was reported by Powers &Sakaguchi [2] the impact strength of PMMA denture base modified by butadiene rubber was doubled in value due to dispersion of rubber particles in the polymer. The addition of rubber particles transformed the characteristic of PMMA denture base material from brittle to ductile material with increase in rubber particles [25]. The function of NBR particles is to promote the energy absorption during the application of fracture force thereby decreasing the crack propagation [2]. Another hypothesis to explain the lowest impact strength value presented [26], they may be due to increase the concentration of cross-linking agent and influence it on the impact strength and increase in flexibility of chain which the material

is weak of polymeric chains. The experimental data and the results were investigated when addition these ceramic filler with PMMA. When ceramic filler was used as reinforced acrylic resin and zirconia as filler in different concentrations with PMMA resin, the result was increase in strength of acrylic resin incorporates with ZrO_2 content to reinforce the strength. The research was carried out using ZrO_2 in two different concentrations (5 wt% and 15 wt%). There was increase of 5% of strength when compared with ZrO_2 at 15 wt% in the mechanical properties [27].

Fig 1(B) shows the fracture toughness (K_{IC}) of 50% Al_2O_3/ 50% YSZ filler with 10 wt% NBR reinforced PMMA matrix compared to PMMA matrix without fillers. The K_{IC} value of PMMA matrix increases from 1.6 to 2.58 MPa.$m^{1/2}$ when reinforced with 5 wt% 50% Al_2O_3/ 50% YSZ filler content than remain the formulations (1,3,7 and 10 wt %). The K_{IC} value of unreinforced PMMA matrix is lower than the PMMA reinforced by 50% Al_2O_3/ 50% YSZ filler with 10 wt% NBR. This is attributed to PMMA matrix was more brittle material which the strength resistance was reduced and the brittle fracture [23]. The K_{IC} value was statistically increased compared to unreinforced PMMA matrix ($p < 0.05$). This shows that the addition of NBR particles has effectively reinforced PMMA denture base materials. In other word, the NBR particles present in the PMMA matrix exhibited ductile fracture and act as impact modifier. It was reported in literature [22, 28] , the strength of PMMA depend on the proportion of addition of a cross-linking agent such as ethylene glycol dimethacrylate bead polymer into the acrylic resin, and also by reinforcement of denture base polymer with rubber phase.

PMMA matrix without filler was lower K_{IC} value compared to another formulation of reinforced PMMA matrix. The different formulations of filler content were added into PMMA matrix, that is, the K_{IC} values were increased up to 5 wt% of filler content. This is due bonding between the filler and PMMA matrix. Another researcher was studied the addition of glass flake by ratios (i.e. 5%, 10% and 20%) into PMMA denture base material. The addition of 5% glass flake lead to an improvement in fracture toughness that was significantly compared to of 10% and 20% which, the lowest percentage loadings were higher in the fracture toughness value compared to the higher loadings. This due to when use high filler loading lead to reduce in homogenous of the mixture and the matrix is weak [29]. Chow et al. [12] determined the reinforcing effect of hydroxyapatite HA on the fracture toughness of PMMA denture base. In additions, 5, 10, 15 and 20% of loading filler HA, the findings were decrease in the fracture toughness. This observation was in agreement with that made [30]; they stated ultimately that an increase in filler fraction does not necessarily lead to an increase in strength as high filler fractions create more defects weakening the material. During these results, it can be concluded that the K_{IC} parameter is more affected by filler content. Therefore, incorporation of a certain amount of composite filler could enhance the properties of the composite.

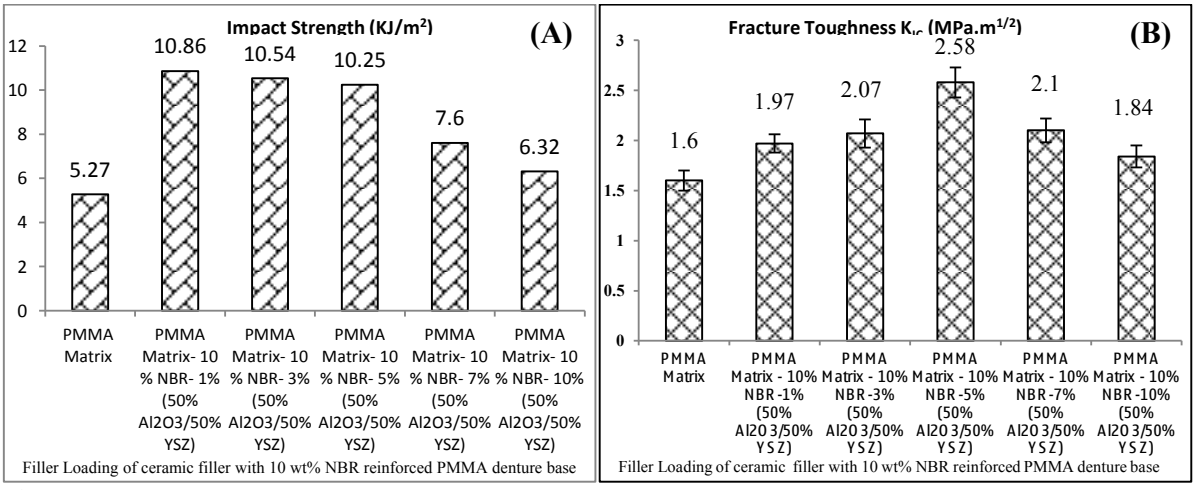

Fig 1. The effect of 50% Al_2O_3/50%YSZ filler loading with 10 wt% NBR reinforced PMMA composites compared to unreinforced PMMA matrix on the impact strength (A) and fracture toughness (B).

5. Conclusion

Within the limitations of the present study, the following conclusions were made: the impact and fracture toughness of heat polymerized PMMA denture base was improved after reinforcement with NBR particles and treated ceramic fillers compared to unreinforced PMMA matrix. The optimum of combination was 10% NBR together with 5 wt% of 50% Al_2O_3/50% YSZ as mixture filler and a suitable combination to improve PMMA denture base properties.

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