Tensile and Shrinkage Evaluation on newly developed β-TCP /ZnO filled PMMA for craniofacial reconstruction

Wan Nur Fadilla Wan Hamad, Abdul Manaf Abdullah, Dasmawati Mohamad*

School of Dental Sciences, Health Campus, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan, Malaysia.

Abstract

Unfilled PMMA suffers from its moderate mechanical properties and high shrinkage. This study aimed to evaluate tensile and shrinkage of newly developed β-TCP/ZnO filled PMMA for craniofacial reconstruction. β-TCP was fixed at 15 wt%, whereas ZnO was varied between 0, 2.5 and 5 wt%. Unfilled PMMA was also prepared as control (n=7/composition). β-TCP particles were in 1-5 µm sizes whereas ZnO particles were in nanosize of less than 260nm.The effect of filler incorporation on the tensile and morphological were determined using Universal Testing Machine (AGX 2 plus, Shimadzu, Japan), field emission scanning electron microscope (FESEM) and scanning electron microscope (SEM). Shrinkage was calculated using volumetric shrinkage formula. Statistical analysis of One-Way ANOVA ($p<0.05$) was employed to assess the differences in the mean of tensile and shrinkage properties between the developed composites and unfilled PMMA. Shrinkage percentages reduced from 8.29 % (unfilled PMMA) to 4.8% with incorporation of 5%ZnO. The tensile strength of the composites was significantly reduced with incorporation of β-TCP/ZnO fillers. Tensile modulus and shrinkage properties of the composites were significantly improved. Thus, this newly developed β-TCP/ZnO filled PMMA is a promising biomaterial for craniofacial reconstruction.

Keywords: β-TCP/ZnO filled PMMA, tensile, shrinkage, craniofacial reconstruction

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*Corresponding author: Dasmawati Mohamad; e-mail: dasmawati@usm.my

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Introduction

Polymethylmethacrylate (PMMA) is one of the most widely accepted thermoplastic material for bone replacement. It has superior advantages such as excellent toughness, stiffness, and transparent to visible light, low thermal conductivity, rigid and good biocompatibility [1]. PMMA has been widely used in dentistry and orthopaedic areas. However, PMMA suffers from its moderate mechanical properties and high shrinkage [2-4].

Shrinkage property is one of the critical issues that need to be encountered to avoid implant loosening after implantation. The loosening of implant is commonly occurred due to bone cement shrinkage. The volumetric shrinkage of acrylates and methacrylates occurs during polymerization due to the replacement of weak long-distance Van der Waals interactions with strong and short covalent bonds between the carbon atoms of different monomer units. This causes a significant accumulation of internal stress which results in defect formation [5]. High shrinkage will not only results in tissue damage [2] but also induce warpage of material which subsequently lead to internal stress. Polymerization shrinkage also affects the dimensional accuracy of the implant [6]. Nishiyama (1998) suggests that the shrinkage can be reduced by introduction of fillers into a polymer matrix [7].

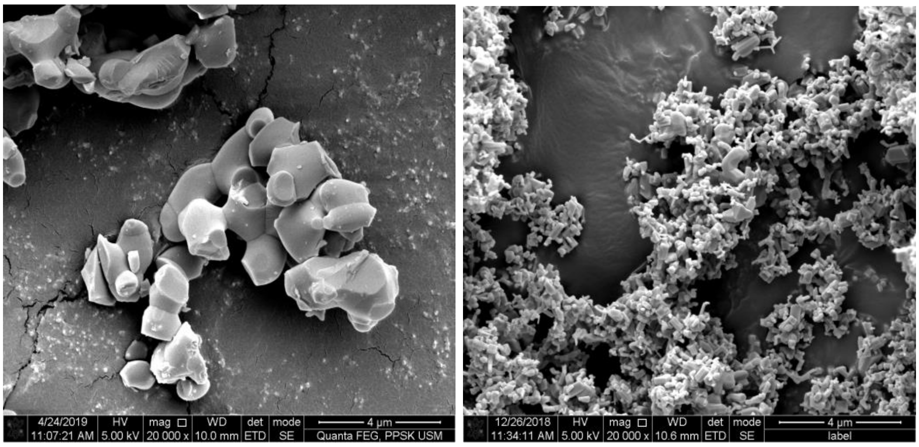
According to Hamizah *et. al.* (2012) the incorporation of bioactive fillers such as hydroxyapatite and β-TCP enhanced the mechanical performance of the PMMA [8]. Besides, β-TCP could induce the formation of bony tissue which could fill the gap between the surrounding bone and apatite layer [8]. In this study, β-TCP was used as a filler due to its excellent osteoconductivity, which could directly bond with the connective tissue and induce rapid bone repair within a few weeks of implantation [9].

Zinc oxide was also used to enhance the mechanical performance of the composites along with the presence of β-TCP. It should be noted that the optical, electrical and mechanical properties of polymer could be modified with addition of ZnO [10]. In this study, the incorporation of β-TCP and ZnO is expected to improve the tensile and shrinkage performance of the developed composites (PMMA filled β-TCP and ZnO) to ensure their longevity.

Materials and Methods

Materials

In this study, Polymethylmethacrylate (PMMA) was purchased from Vertex, Castavaria. Whereas β tricalcium phosphate and zinc oxide where purchased from Sigma-Aldrich and Nacalai Tesque respectively. The particles size of β-TCP and ZnO were 1-5µm and less than 260nm respectively and are shown in Figure 1.



a) b)

Figure 1: FESEM image of a) microparticles of βTCP b) nanoparticles of ZnO at 20 000x magnification.

Preparation of silicone mould

Silicone in viscous form was poured into a rectangular plastic container to form a base layer. 3D printed tensile template with a dimension of 140mm x 20mm x 3.2 mm [11] as well as bar shape template for shrinkage evaluation were embedded into the silicone and was left harden for 1 hour. Then another layer of silicone as an upper layer was applied to the initial harden layer. The upper layer was left harden for another 1 hour. The upper layer of the silicone was prepared to ensure no bubble entrapped during the polymerization of the PMMA.

Preparation of tensile and shrinkage specimen

PMMA composites were prepared by initially mixed the PMMA powder with respective fillers. Liquid monomer was added into powder part and stirred for 20 seconds until homogenous paste was ready. Liquid to powder ratio used was 1.7g/1ml which in accordance to the manufacturer guideline. The paste was then poured to the dumbbell shape mould and bar shape mould and left harden for 8 minutes. First the mould was covered with an upper layer of silicone mould, then covered with gypsum green stone as a clamp to obtain a flat shape of specimen, Figure 2. Lastly, the mould was put in pressure pot for 30 minutes at 2 bar for further polymerisation. The composition of the developed composites was summarized in Table 1. Total samples prepared for tensile and shrinkage evaluation, were 42 samples, which was n=7 per group. Figure 3 showed the example of dumbbell shape of PMMA composite sample for tensile test. The developed composites were fabricated in different ratio of zinc oxide and fix of 15%βTCP as mentioned in Table 1.

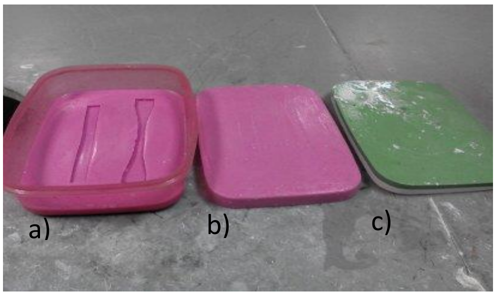


Figure 2: a) Base silicone mould with a tensile dimension b) upper layer of silicone c) gypsum green stone

Table 1: Description of specimens.

Specimens	PMMA (wt%)	βTCP(wt%)	ZnO(wt%)
Unfilled PMMA	100	0	0
PMMA/15%βTCP	85	15	0
PMMA/15%βTCP/2.5%ZnO	82.5	15	2.5
PMMA/15%βTCP/5%ZnO	80	15	5

Figure 3: Tensile specimen fabrication

Characterization of developed PMMA composites

Shrinkage properties

Shrinkage evaluation was carried out using bar shaped specimens, n=7 per composition. Measurement of specimens were taken after cured. The shrinkage calculation was followed by an equation below:

Shrinkage = (Vm-Vs)/Vm x 100 Equation 1

where Vm is the volume of mould (mm^3) and the Vs is the volume of specimen (mm^3)

Tensile properties

The tensile test was carried out using a universal testing machine (AGX-2plus, Shimadzu, Japan). The gauge length was set at 70mm. The test was performed at a cross head speed of 10mm/min. The specimen was tested for n=7/composition and average values were taken.

Morphology evaluation of fractured PMMA composites

A representative specimen of fractured tensile samples from each composition was chosen. The morphology of the specimen was then observed using a field emission scanning electron microscopy (FESEM) (Quanta 450, FEG) following gold coating preparation.

Statistical analysis

Statistical of One Way Anova followed by *post-hoc* Tukey's test was performed to determine the mean differences in shrinkage and tensile properties of four groups. The significant level was set at $p<0.05$. The analysis were performed using SPSS software version 24.

Results and Discussions

Shrinkage properties

Table 2 shows the shrinkage properties of the developed composites. The shrinkage percentage was reduced with the addition of βTCP. However, the value slightly increased with addition of 2.5% ZnO. A statistically significant difference in shrinkage properties was only detected in PMMA/15%βTCP/5%ZnO in comparison to unfilled PMMA.

Table 2: Shrinkage value of unfilled PMMA and developed composites.

Samples	Shrinkage percentage (%)
Unfilled PMMA	$8.29\ (3.81)^{a}$
PMMA +15% βTCP	$5.51(0.74)^{ab}$
PMMA+βTCP 15%+ZnO 2.5%	$6.09(1.23)^{ab}$
PMMA+βTCP 15%+ZnO 5%	$4.80\ (0.55)^{b}$

Mean values and standard deviation in parentheses. Different small letters in the same column are statistically significant according to pairwise comparison test

The shrinkage of PMMA is attributed to the release of volatile products originating from side chain scissions [12]. Polymerization shrinkage occurs when the contraction and expansion started. It started immediately upon initiation of the polymerization and continues along with the curing. Conversion of van de Waals distances to covalent bond will result to contraction effect. In addition, after polymerization, thermal expansion and conversion of double bond to single bond occurred as a result of expansion effect. This is due to the bonding of van der walls strengthen the compound bond, thus reduce void and shrinkage. Besides, shrinkage of polymer occurred when there is an internal rearrangement of the structural elements within stretched sample [13].

The lowest shrinkage percentage was at recorded at the highest filler loading (PMMA/15%β-TCP/5%ZnO). Lai *et al* [14], found that the utilization of monomer with high molecular weight and high filler loading, could lead to less shrinkage. Besides, incorporation of-nanofillers into composites could also reduce the shrinkage due to reduction of resin fraction in shrinkable monomer [15]. Pefferkorn [16] stated that incorporation of organic and inorganic fillers will reduce the polymerization contraction.

Tensile properties

The tensile properties of unfilled PMMA and PMMA composites are summarized in Table 3. Unfilled PMMA recorded the highest tensile strength of 46.98% MPa. The addition of β-TCP and ZnO reduced the tensile strength value. Meanwhile, the tensile modulus of PMMA/BTCP/ 5%ZnO composites were significantly increased (1394.49 MPa) as compared to unfilled PMMA (985.71 MPa).

TABLE 3.Tensile strength and modulus value of each sample.

Sample Name	Tensile strength (MPa)	Tensile modulus (MPa)
Unfilled PMMA	46.98174286 (6.02)[a]	985.71 (370.94)[a]
PMMA/15%β-TCP	32.11444286 (7.51)[b]	1239.71(327.07)[a]
PMMA/15%β-TCP /2.5%ZnO	32.52637143 (7.24)[b]	1299.99(262.07)[a]
PMMA/15%β-TCP /5%ZnO	31.34582857 (5.91)[b]	1394.49(191.59)[b]

Mean values and standard deviation in parentheses. Different small letters in the same column are statistically significant according to pairwise comparison.

The reduction of the tensile strength with addition of β-TCP filler could be due to nonchemical treatment of the filler. Similarly, Kwon *et al* (1997) and Salahuddin *et al* (2018) stated that untreated filler will decrease the performance of the mechanical properties due to weak adherence of the fillers to the matrix resulted in weak bonding [17, 18]. Their study also found that the mechanical properties decreased with the increasing filler content. The reduction in tensile properties with addition of filler was in accordance to our previous study [19] on flexural strength which also showed a reduction in the properties with addition of filler.

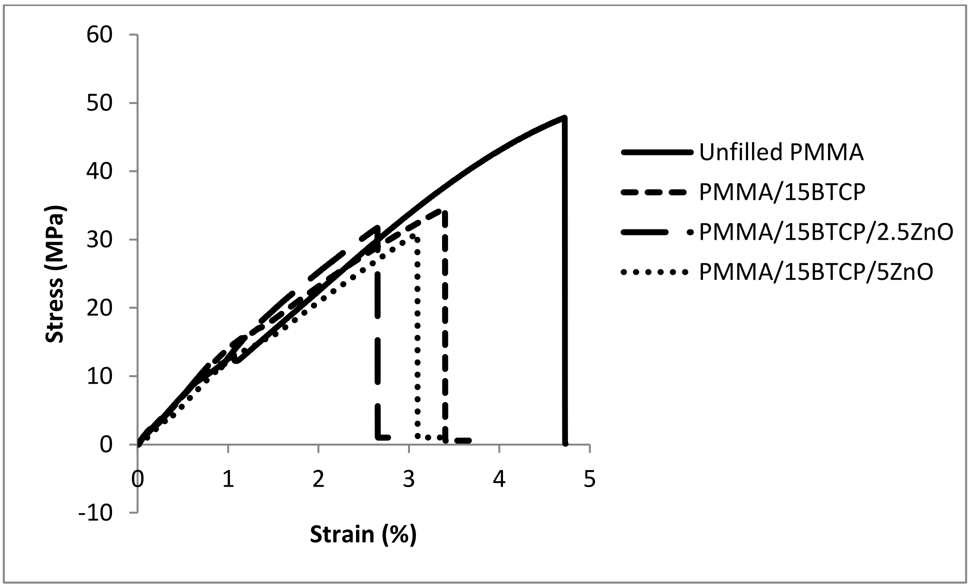


Figure 4: Stress strain curves of unfilled PMMA and developed composites

Figure 4 demonstrated the behaviour of the unfilled PMMA and developed composites. The additional forces caused the unfilled PMMA to elongate close to 5% before fractured. With the increment of filler loading, the strain was decreased to below than 4 %. The lowest strain was detected in PMMA composites with incorporation of 15% β-TCP and 2.5% ZnO. The curves of the composites were relatively steeper than unfilled PMMA which attributed to the increment of modulus of the composites. However, the area under the curve clearly indicates that the incorporation of fillers slightly reduced the ability of the material to withstand the external impact which resulted in moderate toughness.

Morphology evaluation

The morphological properties of fractured unfilled PMMA and developed composites are showed in Figure 5. The unfilled PMMA exhibited a rough surface, Fig 5 (a). The particles were well distributed in polymer matrix, Fig 5 (b). Filler pull out could be observed in Fig 5 (c). β-TCP represented as bulky particles whereas ZnO seen as tiny particles. The presence of void in Fig 6 (b) (PMMA/15%BTCP/5%ZnO) induced the crack propagation, hence reduced the tensile strength.

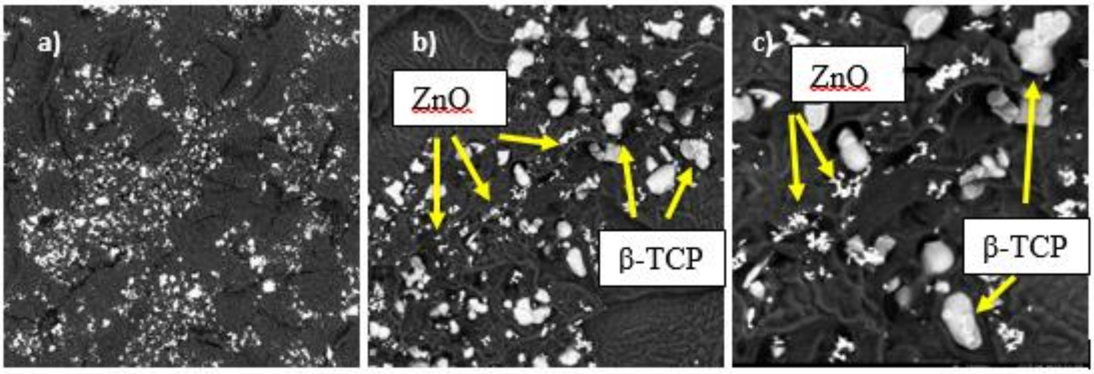


Figure 5: SEM microstructure of fractured PMMA/15βTCP/2.5ZnO at a)1000x b)5000x and c)10000x magnification.

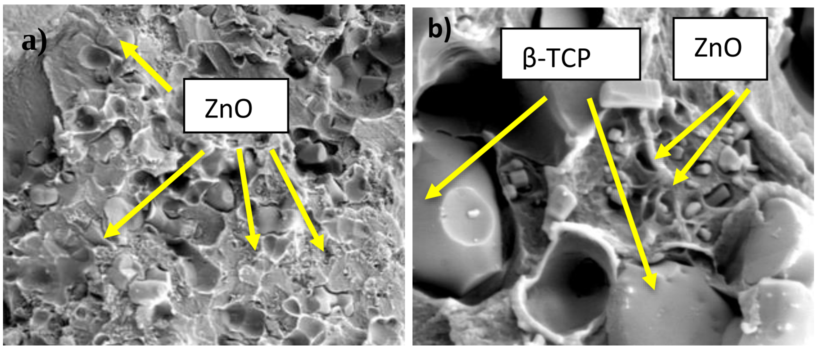


Figure 6: FESEM microstructure of fractured PMMA/15%βTCP/5%ZnO at a) 10 000x b) 50000x magnification.

Conclusion

The shrinkage and tensile properties of PMMA with incorporation of β-TCP and ZnO was successfully evaluated. The addition of filler reduced the shrinkage properties. The lowest shrinkage value was attained with incorporation of 15% β-TCP and 5% ZnO. Even though the tensile strength reduced with addition of filler, the modulus showed significant improvement. With improved shrinkage properties and tensile modulus, this newly developed PMMA composite could be a potential candidate for craniofacial bone application.

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Author Contributions

All authors contributed in designing the study, experimental works, data analysis and critically revising the paper.

Disclosure of Conflict of Interest

The authors have no disclosure to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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