

Effect of Filler Incorporation on the Fracture Toughness Properties of Denture Base Poly(Methyl Methacrylate)

N. W. Elshereksi^{1*}, S. H. Mohamed¹, A. Arifin² and Z. A. Mohd Ishak²

¹Higher Institute of Medical Technology, P.O.Box: 1458, Misurata,-Libya

²School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

*Corresponding author: nidalwanis@gmail.com

Abstract: *Poly(methyl methacrylate) (PMMA) is the material of choice for denture base construction. In spite of its many good qualities, the application of PMMA as an ideal dental base material is still restricted by a few limitations. One of these is the difficulty in achieving intrinsic radiopacity in the material. The aim of the present study is to investigate the possibility of using barium titanate (BaTiO₃) as a radiopacifier in PMMA. The formulation used in this study composed of PMMA 89.5 wt%, BaTiO₃ 10 wt% and benzoyl peroxide (BPO) 0.5 wt% as an initiator, methyl methacrylate (MMA) 90 wt% as a monomer and ethylene glycol dimethyl acrylate (EGDMA) 10 wt% as a cross-linking agent. The BaTiO₃ was treated by a silane coupling agent, 3-trimethoxysilylpropyl methacrylate (γ -MPS), prior to incorporation in the solid components (PMMA, BPO). The curing was carried out using a water bath at 78°C for 1.5 h. The samples were tested for fracture toughness before and after soaking for 28 days in simulated body fluid (SBF). Moreover, the morphology of the specimens was investigated by scanning electron microscope (SEM). The results showed that the neat PMMA possessed slightly higher fracture toughness properties than the PMMA composite, and after 28 days of immersion, the fracture toughness values were reduced by 4.8% and 3.4% for neat PMMA and PMMA composite, respectively.*

Keywords: poly(methyl methacrylate), barium titanate, fracture toughness, simulated body fluid, denture base materials

Abstrak: *Poli metakrilat (PMMA) ialah bahan asas yang menjadi pilihan dalam pembuatan gigi palsu. Namun, ianya mempunyai beberapa kekurangan, antaranya ialah sukar mencapai radiopaque intrisik dalam bahan. Tujuan kajian ini ialah untuk menyelidik penggunaan barium titanat (BaTiO₃) sebagai bahan radiopalegap di dalam PMMA bagi bahan asas gigi palsu. Formulasi yang digunakan dalam peratus berat ialah 89.5% PMMA, 10% BaTiO₃ dan 0.5% benzol peroxida (BPO) sebagai pemula, 90 % metil metakrilat (MMA) sebagai monomer dan 10% etilena glikol dimetil akrilat (EGDMA) sebagai agen penyambung-silang. BaTiO₃ telah diolah dengan agen gandingan silana, 3-trimetoksisililpropil metakrilat (γ -MPS), sebelum pengabungan ke dalam komponen pepejal (PMMA, BPO). Pematangan dilakukan dengan rendaman air pada 78°C selama 1.5 jam. Sampel telah diuji kekukuhan retakan sebelum dan selepas rendaman 28 hari di dalam simulasi bendalir badan (SBF). Morfologi dikaji dengan mikroskop imbasan elektron (SEM). Keputusan menunjukkan bahawa PMMA tulen mempunyai sifat kekukuhan retakan yang agak tinggi berbanding dengan komposit*

PMMA, dengan pengurangan nilai masing-masing sebanyak 4.8% dan 3.4% bagi PMMA tulen dan komposit PMMA selepas 28 hari rendaman.

Kata kunci: poli(metal metakrilat), barium titanat, kekukuhan patah, simulasi bendalir, bahan asas gigi palsu

1. INTRODUCTION

PMMA is used in a wide variety of medical and dental applications and has exhibited excellent biocompatibility when in its bulk, polymerised form.¹ However, this material does not possess the ideal requirements, namely a good combination of mechanical and biological characteristics, required for dental materials.² Dentists and manufacturers of denture base materials have long been searching for ideal materials and designs for dentures. So far, the results have been noteworthy although there are still some physical and mechanical problems with these materials.³

Currently, acrylic resin (PMMA) is used almost universally for denture base construction. Untreated, it is a clear, glass-like polymer and is occasionally used in this form for denture base construction. It is more normal, however, for manufacturers to incorporate pigments and opacifiers in order to produce a more life-like denture base.⁴ The cured polymer should be stiff enough to hold the teeth in occlusion during mastication and to minimise uneven loading of mucus underlying the denture. The denture material should not creep under masticator loads if good occlusion is to be maintained and must have sufficient strength and resilience to withstand normal masticator forces.⁵ Some products have been developed, however, in which attempts have been made to improve the mechanical and environmental properties. Our approach to enhancing the properties of denture base materials and their behaviour in aqueous environments is to incorporate BaTiO₃ filler to act as radiopacifier. Currently, most denture plastics are radiolucent, and concern exists about the difficulty of removing fragments of dentures aspirated during accidents. Radiopacity is often achieved by the addition of a contrast agent, like barium titanate (BaTiO₃).

Denture base acrylic resins are subjected to many different types of stresses. Intra-orally, repeated masticatory forces lead to fatigue phenomena, while high-impact forces may occur extra-orally as a result of dropping the prosthesis. As a consequence, a fracture of the denture base can result. A fracture of denture base in situ often occurs via a fatigue mechanism in which relatively small flexural stresses over a period of time eventually lead to the formation of small cracks that propagate through the denture, resulting in fracture. Additionally, denture fracture is also generally related to faulty design, fabrication, and material choice. Zappini et al.⁶ compared the impact test results

of seven heat-polymerised denture base resins with the results from fracture toughness tests and showed that impact testing is influenced by loading conditions and specimen geometry. Fracture toughness tests may be more suitable than impact strength measurements for demonstrating the effects of resin modifications. The aim of this study is to produce a denture base material with well balanced properties, to evaluate the influence of BaTiO₃ on fracture toughness properties, and to study the effect of simulated body fluid (SBF) on fracture toughness.

2. EXPERIMENTAL

2.1 Materials

The solid components consisted of PMMA with a high molecular weight ($M_n = 996000$ g/mol, Aldrich, USA) and benzoyl peroxide (BPO) (Merck Chemical, Germany). The liquid component was methyl methacrylate (MMA) (Fluka, UK), stabilized with 0.0025% hydroquinone, the cross-linking agent (10%) ethylene glycol dimethacrylate (EGDMA) (Aldrich, USA) and toluene. BaTiO₃ powder (Across, USA) with particle sizes ranging from 0.4 to less than 1 μm was used as filler. The silane coupling agent 3-(trimethoxysilyl) propyl methacrylate (γ -MPS), also known as 3-(methacryloxy) propyl trimethoxysilane, was supplied by Sigma-Aldrich. γ -MPS has a boiling point and flash point of 190°C and 92.22°C respectively, and it enhances the interaction between the ceramic filler (BaTiO₃) and the PMMA matrix.

2.2 Sample Preparation

BaTiO₃ treatment was performed according to the method described by Abboud et al. using 200 ml of toluene and 10 g of BaTiO₃ powder.⁷ After dispersing the powder in toluene, 10 wt% of silane was added and the resulting solution was refluxed for 15 h. The modified powder was then washed with 200 ml of fresh toluene in a Soxhlet apparatus for 24 h. The final powder was dried at 110°C for 3 h under vacuum.

A ratio of 10% by weight of treated filler was added to the matrix (PMMA and 0.5% BPO). The planetary ball milling technique was employed to mix the solid phase (PMMA, BPO and filler) for 30 min. The milling was stopped every 3 min during the run time and continued 4 min later to prevent overheating and premature polymerisation. The ceramic jars and balls must be cleaned by sand several times for 30 min to reduce the contamination of powder mixture. The mixing of powder to liquid (P/L) was done according to standard dental laboratory usage. After reaching the dough stage, the mix was packed into

a mould and pressed under 14 MPa at room temperature for 30 min. The final polymerisation (curing process) was carried out using a water bath at 78°C for 1.5 h. The mould was left to cool slowly at room temperature. The samples were then removed and polished. The procedures adopted in this study were consistent with those of the prescribed standard method for preparing a conventional denture base in the dental laboratory.⁴

2.3 Methods

2.3.1 Fracture Toughness Test

The fracture toughness was determined using the single edge notch bending test (SEN-B) according to ISO 13586:2000. The test specimens were formed in moulded plates (thickness $B = 4$ mm; width, $W = 20$ mm; span length, $L = 64$ mm; overall length, $= 80$ mm; and notch length, $a = 4$ mm). A natural crack was generated by tapping on a new razor blade placed in the notch. The SEN-B specimens were tested at a crosshead speed of 1.00 mm/min. The values for fracture toughness (K_{IC}) were calculated using the following equation:

Geometrical correction factor (y) =

$$1.93 - 3.07 (a/w) + 14.53 (a/w)^2 - 25.11 (a/w)^3 + 25.8 (a/w)^4$$

where,

P = load at peak (N),
 S = span length (mm),
 a = notch length (mm),
 t = specimen thickness (mm)
 w = specimens width (mm).

2.3.2 Fracture Toughness Determination After Immersion in SBF

The samples were immersed in simulated body fluid at 37°C in a water bath and tested after 28 days. Then, the outer surfaces of the samples were manually dried with soft tissue paper, and fracture toughness tests were performed according to the procedures discussed in section 2.3.1.

2.3.3 Scanning Electron Microscopy (SEM)

The morphology of the fracture surface of the composites was studied using SEM with a Leica model Cambridge S-360 microscope. All surfaces were gold coated to enhance image resolution, avoid electrostatic charging and obtain better image resolution.

3. RESULTS AND DISCUSSION

3.1 Fracture Toughness (K_{IC})

Fractures in an acrylic denture base are a common clinical problem. Fatigue failure does not require strong biting forces as relatively small stresses caused by mastication over a period of time can eventually lead to the formation of a small crack, which propagates through the denture and results in a fracture. The maximal biting forces of a patient can reach up to 700 N, but these values are reduced (100–150 N)⁸ with the removal of dentures. Denture fractures are essentially due to stress concentration and increased flexing.⁹

Figure 1 shows the K_{IC} of a BaTiO₃ filled PMMA matrix. It should be noted that PMMA by itself possesses slightly higher fracture toughness properties than does the PMMA composite. This is because the adhesion of the PMMA matrix to BaTiO₃ is slightly weak due to partial embedding of the BaTiO₃ filler in the PMMA matrix itself. Moreover, the anisotropic particle orientation throughout the composite also increases the resistance against local plastic deformation, making the composite more brittle. Thus, crack propagation will be very quick due to the inability of the composite to absorb energy through plastic deformation. Similarly, Bonilla et al.¹⁰ reported a very weak correlation between fracture toughness and filler content. They observed that although the filler type, distribution and composition had a strong effect on fracture toughness, the properties of the polymer matrix may also contribute to enhance K_{IC} . Schulze et al.¹¹ concluded that an increase in filler fraction does not necessarily lead to an increase in strength. This is because higher filler fractions create more defects that weaken the material.

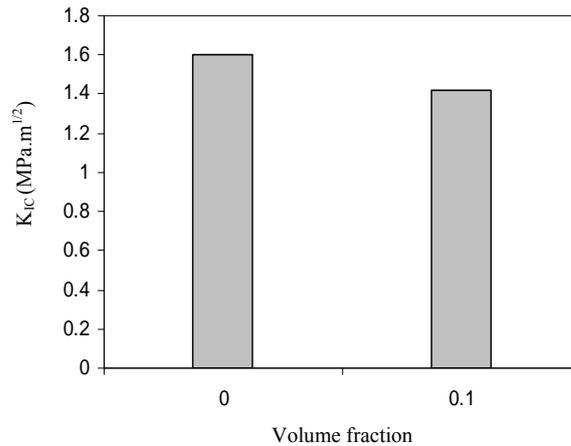


Figure 1: Effect of filler content on the fracture toughness of the PMMA matrix containing 10 wt% BaTiO₃.

3.2 The Effect of SBF Exposure on Fracture Toughness

The mechanical properties of denture-base polymers could be affected by an aqueous environment in the long term.¹² Figure 2 shows the effects of SBF on the fracture toughness of various formulations of denture base materials. The PMMA matrix revealed a decreased in fracture toughness by 7.9%, 6.6% and 4.8% after 1, 14 and 28 days of immersion in SBF, respectively. It should also be noted that there occurred a slight reduction in fracture toughness for the PMMA composite after it was immersed in SBF. However, there was very little difference in fracture toughness values amongst the PMMA composites during the immersion period. In fact, the values decreased by 1.4%, 2.7% and 3.4%. This is due to an increase in the hydrolytic degradation of the silane coupling agent, causing a filler-matrix debonding.¹³ In addition, the SBF molecules can be accommodated at the interface between the filler and the matrix through a weak link. This weak link could provide paths of facile diffusion towards the innards of these aggregates in which filler particles and the polymer matrix are present. Nevertheless, the mechanical properties of the filled samples were degraded after the absorption-desorption cycles were completed. This finding is consistent with that of Deb et al.¹⁴ who reported that the uptake of water can lead to a reduction in polymer strength. It is interesting to note that this finding is also in agreement with Calais and Söderholm,¹⁵ who found that composites containing barium were significantly weaker after three months of immersion in water compared to any other investigated time interval. Ferracane and Berge¹⁶ reported that aging in ethanol caused a reduction in K_{IC} values for the composites.

The effect of an aqueous environment on the K_{IC} of composites has been studied by a number of investigators. Lassila et al.¹² found that the interface between the polymer matrix and the fibres could be affected by contact with an aqueous environment in the long term. Varying results have been reported, with some results indicating a decrease in K_{IC} .^{17,18} Pilliar et al.¹⁹ observed that K_{IC} generally decreased after aging dental composites in water at 37°C for periods of one month or more. In contrast, others show an increase in K_{IC} .^{20,21} Yet, there are other results that reported no significant difference in K_{IC} between composites stored in air or in water.^{10,22}

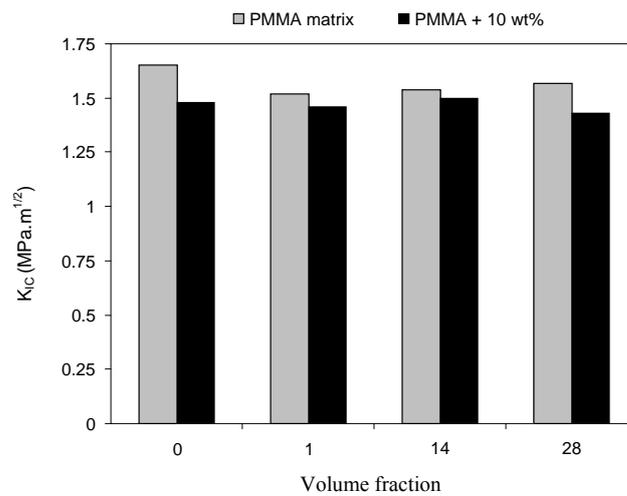


Figure 2: Effect of SBF exposure on fracture toughness of the PMMA matrix filled with BaTiO₃ compared to the PMMA matrix after immersion in SBF at 37°C.

3.3 Scanning Electron Microscopy (SEM)

Figures 3 and 4 show the fracture surface of a BaTiO₃-filled PMMA matrix, and the PMMA matrix after a fracture test was conducted. Figure 3 shows the fracture surface of the PMMA matrix at a magnification of 2000X. The crack propagated from the initiation site creating a striped pattern, clearly signifying the occurrence of stable crack propagation. Subsequently, the fracture morphology appeared smoother, indicating indiscriminate crack propagation through the PMMA matrix.

Figure 4 displays the fracture surfaces of a BaTiO₃-filled PMMA matrix (10 wt% filler loading). A stable crack propagation state can be seen in the fracture surface. The interaction between the filler and PMMA matrix was relatively strong, and the fracture surface was considerably rougher. The increase

in roughness implies the occurrence of a longer crack path and the release of greater fracture energy. Such an appearance is often associated with brittle failure. The filler particle is observed to be embedded and semi-bonded to the matrix. This indicates that the filler-matrix interaction was relatively strong, allowing debonding to occur prior to the full development of plastic deformation. This is in agreement with Leong²³ who found that talc has a tendency to agglomerate at higher filler loadings, causing the deformability and toughness of PP composites to decrease substantially. The effect of higher filler loading in reducing matrix deformation has also been documented by other researchers.²⁴

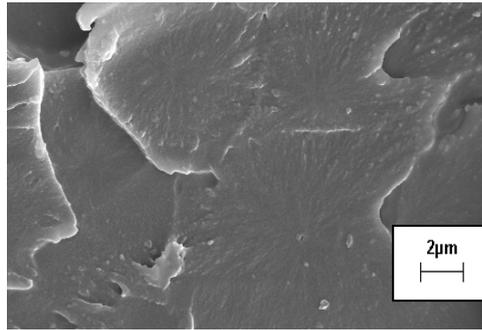


Figure 3: SEM micrograph of the fracture toughness surfaces of the PMMA matrix at a magnification of 2000X.

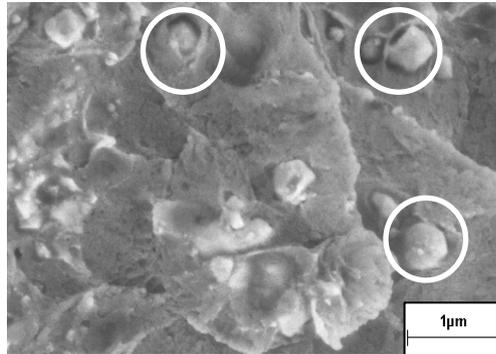


Figure 4: SEM micrograph of fracture toughness surfaces of the 10 w% (BaTiO₃-filled) PMMA matrix at 10000X. The filler particles are surrounded by white circles.

Figures 5 and 6 display the fracture surface of unfilled PMMA and BaTiO₃-filled PMMA specimens after immersion in SBF for 28 days. The unfilled sample (Fig. 5) shows a smooth surface, with no bead detachment. This contributed to rapid crack growth and stable crack propagation, resulting in a slightly lower K_{IC} value for immersed pure PMMA samples compared to those exposed to air. Figure 6 shows the fracture surfaces of 10 wt% BaTiO₃-filled

PMMA matrix where the fracture surface seems to be rougher. It can be also seen that the filler particles in the fracture surface were partially debonded from the matrix even after the fracture process. This may be attributed to poor interaction between the BaTiO₃ and the PMMA matrix.

However, after the filler particle fractures, the matrix must absorb the load in that region, and a crack propagates to adjacent filler particles. This means that the stress level in the surrounding filler particles suddenly increases, and cracks propagate from surface flaws within these particles. Similar observations were reported by Söderholm²⁵ and Söderholm et al.²⁶ The bond between the filler and matrix is essential to the longevity of the material. Should a bond failure occur between the filler and the matrix, as it may occur in an aqueous environment, the strength of the composite will decrease. The finding is that the BaTiO₃-containing composite was notably weaker after immersion in SBF compared to the pure PMMA. A possible explanation could be that at this time the samples were not completely saturated with water, and that such an incomplete saturation results in local stresses. These stresses, as well as the weakening effect of water on the resin matrix, could explain why this minimal strength was found.¹⁵

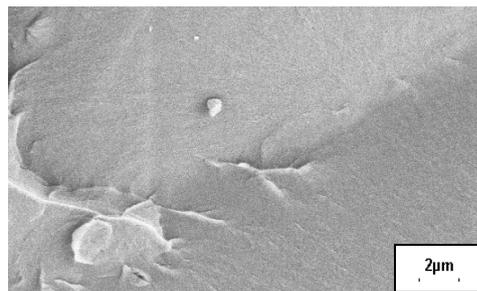


Figure 5: SEM micrograph of fracture toughness surfaces of the PMMA matrix after 28 immersion days at 2000X.

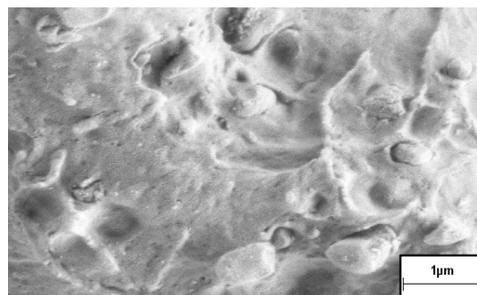


Figure 6: SEM micrograph of fracture toughness surfaces of the 10 wt% (BaTiO₃-filled) PMMA matrix after 28 immersion days at 10000X.

4. CONCLUSION

The general behaviour of the tested materials showed that the dry samples provided higher values of fracture toughness while the wet ones generated the lower values. However, when the composite was exposed to SBF, two detrimental effects will occur. First, the liquid destroyed some of the filler-matrix bonds, resulting in an irreversible reduction in fracture toughness. Second, the liquid caused the surrounding matrix to swell and plasticise, thus reducing the hoop stress around the filler particles and facilitating filler pull-out. If a crack is generated in the matrix when the swelling exceeds its elongation to break then the process is irreversible. Consequently, the composite will not recover its original properties. In addition, it is interesting to mention that the aqueous environment played a major role in filler-matrix bond failure. Generally, the fracture toughness of denture base materials was significantly changed after immersion in SBF.

5. ACKNOWLEDGMENTS

The authors would like to thank the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia for supporting this work.

6. REFERENCES

1. Gilbert, J.L., Nay, D.S. & Lautenschlager, E.P. (1995). Self-reinforcement composite poly(methyl methacrylate): Static and fatigue properties. *J. Biomater.*, 16, 1043–1055.
2. Dennis, B., Smith, C., David, S. & Williams, F. (2000). Biocompatibility of dental materials, IV, 124–130.
3. Memon, M. S. (1999). *An evaluation of some properties of heat and microwave polymerized denture base resins*. Diss. M.Sc., University of Malaya, 3–4.
4. McCabe, J. F. & Walls, A. W. G. (2002). *Applied dental materials*, (8th ed.). London: Blackwell Science Ltd, Ch. 13, 96–106.
5. O' Berry, W. J. (1997). *Dental materials and their selection* (2nd ed.) USA: Quintessence Books Co, 87.
6. Zappini, G., Kammann, A. & Wachter, W. (2003). Comparison of fracture tests of denture base materials. *J. Prosthet. Dent.*, 90, 578–85.
7. Abboud, M., Vol, S., Duguet, E. & Fontanille, M. (2000). PMMA-based composite materials with reactive ceramic fillers, part III. Radiopacifying particle-reinforced bone cements. *J. Mater. Sci. Mater.*, 11, 295–300.

8. Narva, K. K., Lassila, L. V. J. & Vallittu, P. K. (2005). Flexural fatigue of denture base polymer with fiber-reinforced composite reinforcement. *J. Compos. Part A*, 36, 1275–1281.
9. Franklin, P., Wood, D. J. & Bubb, N. L. (2005). Reinforcement of poly (methyl methacrylate) denture base with glass flake. *J. Dent. Mater.*, 21, 365–370.
10. Bonilla, E. D., Yashar, M. & Caputo, A. A., (2003). Fracture toughness of nine flowable resin composites. *J. Prosthet. Dent.*, 89, 261–267.
11. Schulze, K. A., Zaman, A. A. & Söderholm, K. J. M. (2003). Effect of filler fraction on strength, viscosity and porosity of experimental compomer materials. *J. Dent.*, 31, 373–382.
12. Lassila, L. V. J., Nohrstrom, T. & Vallittu, P. K. (2002). The influence of short-term water storage on the flexural properties of unidirectional glass fibre-reinforced composites. *J. Biomaterials*, 23, 2221–2229.
13. Santos, C., Clarke, R. L., Braden, M., Guitian, F. & Davay, K. W. (2002). Water absorption characteristics of dental composites incorporating hydroxyapatite filler. *J. Biomater.*, 23, 1897–1904.
14. Deb, S., Braden, M. & Bonfield, W. (1995). Water absorption characteristic of modified hydroxyapatite bone cement. *J. Biomater.*, 16, 1095–1100.
15. Calais, J. G. & Söderholm K. J. M., (1988). Influence of filler type and water exposure on flexural strength of experimental composite resins. *J. Dent. Res.*, 67(5), 836–840.
16. Ferracane, J. L. & Berge, H. X. (1995). Fracture toughness of experimental dental composites aged in ethanol. *J. Dent. Res.*, 74(7), 1418–1423.
17. Kim, K. H., Park, J. H., Imai, Y. & Kishi, T. (1994). Microfracture mechanism of dental resin composites containing spherically-shape filler particles. *J. Dent. Res.*, 37, 499–504.
18. Drummond, J. L., Andronova, K., Al-Turki, L. I. & Slaughter, L. D. (2004). Leaching and mechanical properties characterization of dental composites. *J. Biomed. Mater. Res. Part B* 71B(1), 172–180.
19. Pilliar, R. M., Smith, D. C. & Maric, B. (1986). Fracture toughness of dental composites determined using the short-rod fracture toughness test. *J. Dent. Res.*, 65(11), 1308–1314.
20. Lloyd, C. H. & Mitchell, L. (1984). The fracture toughness of tooth coloured restorative materials, *J. Oral Rehabil.*, 11:257–272.
21. Lloyd, C. H., & Adamson, H. (1987). The development of fracture toughness and fracture strength in posterior restorative materials. *J. Dent. Mater.*, 3, 225–231.
22. Pilliar, R. M., Vowles, R., & Williams, D. F. (1987). The effect of environmental aging on the fracture toughness of dental composites. *J. Dent. Res.*, 66(3), 722–726.

23. Leong, Y. W. (2003). *Characterization of talc and calcium carbonate filled polypropylene hybrid composite: Mechanical, thermal and weathering Properties*. Diss. M.Sc., Universiti Sains Malaysia, Pulau Pinang, 146.
24. Wang, M. & Bonfield, W. (2001). Chemical coupled hydroxyapatite-polyethylene composite: Structure and properties. *J. Biomater.*, 22, 1311–1320.
25. Söderholm, K. J. M. (1983). Leaking of fillers in dental composites. *J. Dent. Res.*, 62(2), 126–130.
26. Söderholm, K. J., Zigan, M., Ragan, M., Fischlschweiger, W. & Bergman, M. (1984). Hydrolytic degradation of dental composites. *J. Dent. Res.*, 63(10), 1248–1254.