Influence of Environmental Exposure on Absorption, Solubility and Flexural Properties of α-cordierite Filled Denture Base Poly (Methyl Methacrylate)

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ABSTRACT

The usage of α-cordierite ceramic in denture base poly (methyl methacrylate) as reinforcement is never been reported in open literature. The aim of this study attempted to investigate the effects of α-cordierite on environmental properties of PMMA denture base material, also study the influence of environmental exposure on flexural properties. The α-cordierite was treated with silane coupling agent. According to the standard dental laboratory application, the samples were prepared by adding α-cordierite powder (0, 5, 10, and 15 wt%, respectively) to the MMA monomer and PMMA mixed by hand. The blend at dough stage packed to fill moulds. The samples were tested for environmental properties after soaking for 28 days in water and simulated body fluid. Flexural strength was investigated for PMMA matrix sample and composites samples before and after immersion in water and SBF. The morphology of the specimens was investigated by scanning electron microscope . The results showed that the samples which continued with the treated filler showed higher water

absorption. Also, the absorption of simulated body fluid was found to be more in the samples that contained treated filler. But, the solubility of simulated body fluid was less in the composites samples. The flexural properties in all samples were decreased after immersion.

Keywords: poly (methyl methacrylate), α-cordierite, environmental exposure, flexural strength, simulated body fluid.

Introduction

Denture based material should have many key physical characteristics. Some of these properties include good esthetics, biocompatibility, radiopacity, ease of repair, high bond strength with available denture teeth and should possess suitable physical and mechanical properties. In addition the denture base must be strong enough to allow the prosthesis to withstand functional and parafunctional masticators forces [1]. The most commonly used material for the fabrication of removable dentures base is poly (methyl methacrylate) PMMA. It has many advantages which include simple processing technique, optical properties, economy, color stability, adequate strength, free from toxicity, pigmented and other physical properties which make it the material of choice for the fabrication of denture base [2-3]. Although it is popular, PMMA is still far from ideal denture base materials requirements [4]. It showed that poor mechanical requirements of

prosthesis [5]. Once inside the mouth, poly methyl methacrylate denture base is at risk of facing a lot of different kinds of stresses [6]. Filler incorporation into polymer matrix can effect also in oral cavity, for instance thermal and mechanical properties. Inorganic fillers have a significant role in the thermal stability of the polymer composites through interfacial interaction[7]. Water sorption of filler-reinforced composites has an important role in durability of filler-reinforced dental appliances in an aqueous environment such as in the oral cavity [8]. Polat et al. [9] reported that the uptake of water by resin materials is a diffusion-controlled process. Water molecules diffuse through polymer during the immersion in water or saliva and reach the interface of polymer matrix and reinforcing filler. The radiopacity of composites can be improved by using glass and ceramic fillers [10]. Gladwin and Bagby [11] reported that, ceramic materials are chosen as fillers for their unique

properties. They are due to the fact that strong hard ceramic materials have low coefficients of thermal expansion. When they are mixed with polymers, it will have coefficients closer to tooth structure. Because a composite has small amount percentage of polymers in the system, there is a reduction of polymerization shrinkage when the material sets. Moreover, McCabe and Walls [12] stated that

showed slightly higher fracture toughness properties than the PMMA composite. However, when the composite was exposed to SBF, the liquid destroyed some of the filler-matrix bonds. Thus, a reduction in fracture toughness took place. Pahlavan et al.[13] stated that the ceramic fillers increased the flexural strength and flexural modulus notably. The α-cordierite ceramic powder can also be used as strong filler. It has special properties [14]. The α-

Materials and methods

The solid elements consisted of PMMA with high molecular weight (966,000 GPC– Aldrich U.S.A) plus 0.5% benzoyl peroxide (BPO) (Merck Chemical, Germany). The liquid component comprised of methyl methacrylate (MMA) (Fluka UK), stabilized with 0.0025% hydroquinone plus the cross linking agent

the material used to produce a denture base should have a low value of specific gravity in order that dentures should be as light as possible. Many researchers reported that the incorporation of ceramic powder as a filler can improve the PMMA denture base material. Elshereksi et al.[6] studied the effect of incorporation barium titanate as filler on the composite. They observed that the neat PMMA cordierite has a very high specific resistivity (ρ >1012 _cm), , low specific gravity (~ 2.5 g/cm^3), and stable at elevated temperature [15-17]. The aim of this study is to produce a denture base material with balanced properties, to investigate the effect of α-cordierite on environmental properties, and to study the influence of environmental exposure on flexural strength.

(10%) ethylene glycol dimethacrylate (EGDMA) (Aldrich USA) and toluene. The α-cordierite powder had selected as strengthening filler with average particle size 1.06 µm. The silane coupling agent 3-(trimethoxysily) propyl methacrylate was supplied by Sigma-Adrich. (γ-MPS) has a boiling point of190ºC. It used in this study.

Silane enhances interfacial bonding by providing covalent bonds between the filler and the matrix of the dental composite [18]. 10g of α-cordierite powder and 10 wt% of silane were added into 200 ml toluene. The solution was refluxed for 15h before filtered in order to collect the modified powder. The powder was washed with 200ml of fresh toluene in a soxhelt apparatus for 24h. The final product dried at 110ºC for 3h under vacuum. Filler treatment was done according to the method as reported by [19]. The treated α-cordierite powder was blended with matrix

Water absorption test , Simulated Body Fluid (SBF) absorption test and The solubility test were carried out according to ISO 1567-2001. The weights of samples taken were 0.5-0.6g and the surfaces were smoothed and polished by SiC paper p280 and p1200 respectively. Five specimens were prepared from each formula. The

material (PMMA and 0.5% BPO) with different ratios (0, 5, 10, and 15 wt%, respectively) in a plastic ball mill for 20 min. The blending 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 was pressed under 14 MPa, at room temperature for 30 min. The final polymerization (curing process) was carried out in a water bath at 78ºC for 90 min before the mold was left to cool slowly at room temperature. After that the samples removed.

samples were dried in vacuum oven at 37 ± 2ºC for 24 hours, then the samples were weighted using analytical balance of reading 0.0001g then immersed in distilled water at room temperature and weighted after 1, 7, 14, 21, and 28 days, respectively. The change in weight percentage is calculated by the equation:

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

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

Five specimens were prepared with 5%, 10%, 15% of treated filler and 0 %. After that, samples were immersed in water at room temperature for 28 days and another

five specimens were prepared with 5%, 10%, 15% of treated filler and 0 % also immersed in SBF. The samples surfaces were manually dried with soft tissue paper.

Then, they were tested in 28th day. The flexural test was done According to ASTM D790-86. The support span was set at 50mm whilst the diameter of the loading nose and supports were 20mm and 10 mm, respectively. Tests were conducted at a crosshead speed of 2 mm/min on the Instron 5582 10 KN. The flexural strength was calculated using the following equation:

$$\text{flexural strength} = \frac{3PL}{2bd^2} \qquad\qquad (2)$$

Whereby L = span length, p = maximum load, b = specimen width, and d = specimen thickness.

Results and discussion

Water Absorption

Deb et al. [20] stated that many researchers have defined water absorption phenomenon of several polymeric material, whether filled or not, is of significance for all applications in the body Excessive water uptake may lead to the breakdown of the polymer itself and can also lead to the ingress of microorganisms. The uptake of *1%* water can lead to a decreasing in the strength and the fatigue life of the polymer. Some water absorption is beneficial in dental filling materials, for which the accompanying swelling compensates for the polymerization shrinkage. Water absorption behavior of polymer composites at a particular environmental condition is determined by various factors, such as processing techniques, matrix filler characteristics, composition of the composites, and duration of immersion in water [21]. Water sorption of filler-reinforced composites has and especially in dental and orthopaedic devices and implants. Absorbed water can relieve internal strains and allow the extraction of free monomer or polymerization residues. an important role in durability of filler-reinforced dental appliances in an aqueous environment such as in the oral cavity [8]. Polat et al. [9] reported that the uptake of water by resin materials is a diffusion-controlled process. Water molecules diffuse through polymer during the immersion in water or saliva and reach the interface of polymer matrix and reinforcing filler. It can diffuse through polymer matrix because of the small size of the water molecules which is smaller than the polymer chain distance in the polymer matrix. Water is absorbed into polymer by unbalanced intermolecular forces in the polymers. Figure 1 shows the water absorption values of various

denture base formulations immersed in water at room temperature. It can be clearly noted that the water uptake increasing in all samples with increase filler loading until a constant value after 28 days immersion. The uptake of water has been related to the degradation of the filler-matrix interface and plasticizing of the matrix [22]. The SEM of the samples revealed the presence of porosity and voids and inclusions or filler particle aggregates practically in all the composites. These inclusions might be implicated in the water absorption as they appear loosely embedded in the matrix. Thus, additional amount of water can be accommodated at the interface between these agglomerates and the matrix. This lead to weakness the link between the matrix and filler particles. Moreover, the presence of microvoids is quite probable due to a lack of impregnation of filler particles with the polymer matrix [23]. Another explanation it might be because of the presence of silane coupling agent that inhibited the ability of the filler to absorb water by producing a hydrophobic surface upon the filler [24]. This result is in agreement with one made by Tham et al. [25] who studied simulated body fluid and water absorption effects on PMMA/hydroxyapatite denture base composites. For denture-base polymer, the value of water sorption should be less or equal $32\mu g/mm^3$. Table 1 shows comparing the water absorption values of the composite and the PMMA matrix after 28 days of immersion in water at room temperature. It is clear to note that the water absorption of all PMMA/α-cordierite composites is below the value specified by the ISO standards for denture base materials (1567-2000).
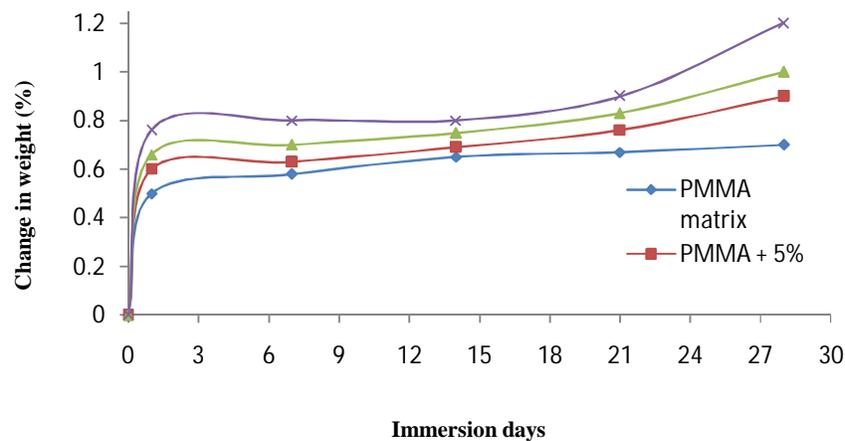

Figure 1: Water absorption curves of α-cordierite filled PMMA matrix compared to that of the PMMA matrix after 28 days immersion at room temperature

Table 1: Water absorption values of the composite compared to that of the PMMA matrix after 28 days immersion in water at room temperature

Formulations	Amount of water absorption (%)	Corresponding of water absorption to ($\mu g/mm^2$)
PMMA matrix	0.85	9.9
PMMA + α-cordierite (5wt %)	0.9	10.75
PMMA + α-cordierite (10wt %)	1	12.17
PMMA + α-cordierite (15wt %)	1.2	14.4

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

Absorption of Simulated Body Fluid

Through clinical use, denture base resin materials are immersed in saliva, and during denture storage they are kept in water or an aqueous cleansing solution. This immersion can lead to absorb the water or saliva by denture base resins [26]. An essential issue regarding the clinical degree of resistance to biodegradation. However, several studies showed that polymers may be subject to a myriad of degradation processes in the oral cavity. Polymer degradation does not occur as a result of isolated processes, multiple factors as saliva, chewing, thermal and chemical dietary changes may be responsible for the biodegradation processes [28-29]. According to Bettencourt et al. [27] who reported that many researches

application of the acrylic based resins is their biodegradation. It can be defined as the changes on their chemical, physical and mechanical properties due to the oral environment conditions [27]. The polymeric materials were classically recognized as large stable structures with a high proved that water is the most abundant component of saliva as such is one of the main factors to cause biodegradation. The oral environment necessarily facilitates water sorption from the saliva to the resin, which is a polar material. There are two conditions that influence the amount of water diffusion to denture resins. One is the water diffusion coefficient of the material that affects the time needed for its saturation with water. The other one is the

amount of residual components that are release for the medium and replaced by water molecules [28 & 30]. Figure 2 shows the absorption of Simulated Body Fluid (SBF) values of PMMA composites compared to that of the PMMA matrix after immersion in SBF at 37 ˚C. It is clearly show that the result is similar to the water absorption result (refer to figure 1). The amount of absorption of SBF increased with increasing in the filler loading.   As mentioned earlier, water is the most component of saliva. Water molecules can easily penetrate the polymer network allowing the diffusion of unbound/uncured monomers and/or additives from the material network. This increase in SBF values can be attributed to that of the water molecules that can penetrate into the spaces between the polymer chains and push them farther apart [27]. As a result of this penetration of water molecules, it can be lead to the lack of a strong interaction between the polymer and the ceramic, leading to void spaces around the PMMA degradation on mechanical properties has been manifested as a reduction in surface hardness and wear resistance [27]. Table 2 shows the SBF absorption values of α-cordierite filled PMMA matrix, and PMMA matrix after 28 days of immersion

composite could be responsible for the faster kinetics of water uptake during the first days, allowing an easier penetration of water through these voids [refer to SEM figure 7 (a)] in a second stage (from 7 to 28 days) the diffusion through the matrix predominates (because the voids are quickly filled) [31]. Consequently, the secondary chemical bonding forces between the polymer chains decline and results in weight and volume increase to cause an expansion. The greater absorption of water by the material, the greater will be the associated dimensional change. Moreover, salivary enzymes can degrade polymers through attacks on the side chains, producing both potentially harmful by-products as well as a deterioration of the properties of the network. The composition of the monomers producing the network is a major factor in determining the extent of degradation, especially when enzymes are responsible [32 & 28]. The effect of enzyme

in SBF at 37 ˚C compared with standards as set by ISO. The SBF absorption for all formulation was below the value as specified by the ISO standard (1567-2000) for denture base materials.
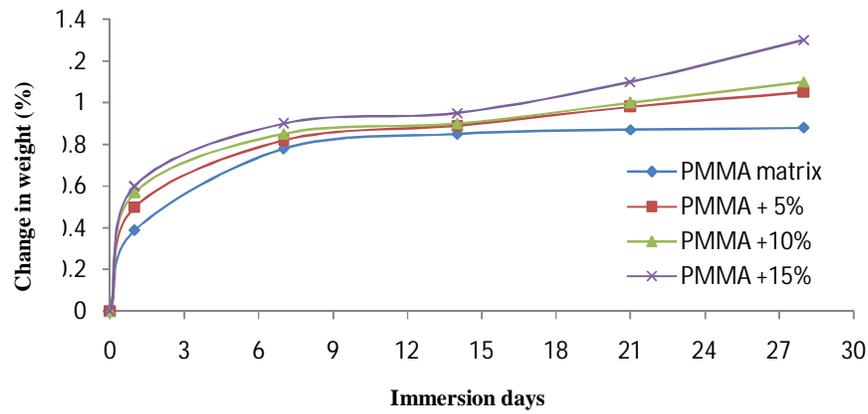
Figure 2: SBF absorption curves of the composite compared to that of the PMMA matrix after 28 days immersion at 37 ˚C

Table 2: The SBF absorption values of α-cordierite filled PMMA matrix compared to that of the PMMA matrix after 28 days immersion in SBF at 37 ˚C

Formulations	Amount of water absorption (%)	Mass weight increase by ($\mu g/mm^2$)
PMMA matrix	0.88	10.1
PMMA + α-cordierite (5wt %)	1.05	12.4
PMMA + α-cordierite (10wt %)	1.1	14.7
PMMA + α-cordierite (15wt %)	1.3	15.8

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

Solubility in Simulated Body Fluid

Dietz-Bourguignon [33] defined the solubility of any material as is the ability of a substance to dissolve in a fluid. In dentistry, the solubility of a dental material is an important factor used to determine the long-term success of a material used in the mouth. Table 3 summarizes the solubility of α-cordierite filled PMMA composite compared to that of the unfilled PMMA after 28 days of immersion in SBF at 37 ˚C. it is clear to note that after the samples which contained the filler showed lower solubility than PMMA matrix samples. 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 [34]. The loss in weight is probably due to the leaching of the residual monomer near the surface of the resin and it is subsequent diffusion into the fluid causing a decrease in the samples weight [35]. Moreover, the residual monomer in PMMA composites could be considered as the sum of both the extractable parts. The extractable part was connected with the surface of the material, which did not reach such high temperature upon polymerization as polymer from the internal part of the material diffused onto its surface. The non-extractable part refers to the molecules trapped in the long polymer chains. Thus, the real 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 [36]. In addition, the solubility of them was decreasing with increasing filler loading. This decreasing in weight loss in treated samples can be attributed to the presence of silane coupling agent on the fillers surfaces which generated a hydrophobic surface. This finding is in agreement with one made by Abudalazez [37] who stated that the treated samples showed lower weight loss than PMMA matrix samples when studied the solubility of composites incorporated with opaque dental porcelain treated with silane coupling agent. Table 3 shows the solubility values of α-cordierite filled PMMA matrix compared of that neat PMMA matrix after 28 days of immersion in SBF at 37 ˚C. It is evident that the solubility values are well below the value specified by ISO standard for denture base materials.

Table 3: The Solubility values of the composite compared to that of the PMMA matrix after 28 days immersion in SBF at 37 ˚C

Formulations	Weight loss by (%)	Mass weight loss by ($\mu g/mm^2$)
PMMA matrix	0.1	1.4
PMMA + α-cordierite (5wt %)	0.09	1.1
PMMA + α-cordierite (10wt %)	0.07	0.56
PMMA + α-cordierite (15wt %)	0.04	0.54

ISO standard (1567-2001) value: max weight loss percentage: 0.99%, max weight increase: 1.6 µg/mm^2.

Effect of Water Exposure on Flexural Strength

As mentioned earlier, water molecules are able to penetrate between the polymer chains in a process called water absorption [38]. Figure 3 illustrates comparing between the samples of PMMA matrix and PMMA/α-cordierite composites before and after immersion in distilled water at room temperature. The samples of all formulation were significantly different in their flexural strength before and after the immersion. The flexural strength of samples was found to decrease after the immersion for 28 days. This is in agreement with Mortensen [39] who stated that water penetration into resin matrix composites can lead to changes in mechanical properties. Moreover, the change is usually associated with deterioration in flexural properties. Reduction of the flexural strength was highest and was likely because of the high-water sorption of the polymer matrix which caused plasticization of the polymer is also probably due to that the weakened adhesion between the polymer matrix and the ceramic filler. This is in agreement with Mohamed [40] who noted the drop in the properties of filled samples was due to corrosion of the silane that promoted the adhesion of the polymer matrix to the

ceramic filler. The main mechanism for the ingress of water is diffusion and some absorption is facilitated by the polarity of polymer chains. Water molecules penetrate

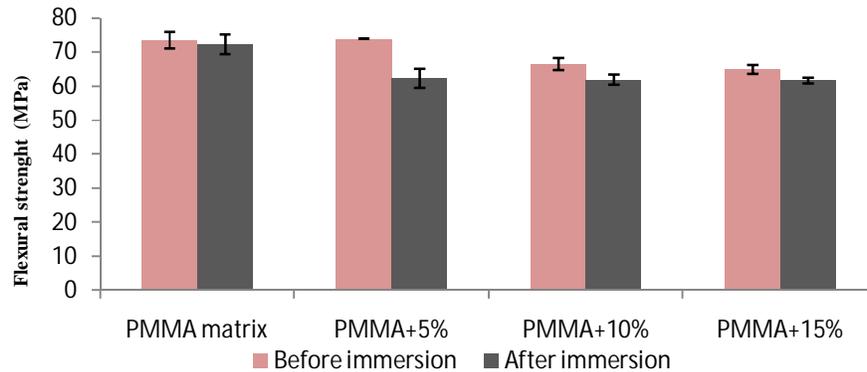occupy positions between the chains, and therefore, the polymer chains are forced apart [41].

Figure 3: Effect of water absorption on flexural strength of PMMA matrix and the composites compared to the same samples before exposure

Effect of Simulated Body Fluid Exposure on Flexural Strength

Figure 4 shows comparing between the samples of PMMA matrix and PMMA/α-cordierite composites before and after immersion in Simulated Body Fluid (SBF) at 37 ˚C. The samples of all formulation were significantly different in their flexural properties before and after the immersion. The flexural strength of samples was found to decrease after the immersion for 28 days with increasing in the filler content. As mentioned earlier, water is the most component in SBF thus the decreasing in flexural strength can attribute to the presence of water which can cause

plasticization of the polymer matrix and deponding at the filler/ matrix interphase. Water molecules induced more new cavities and cracks, thus the interphase was gradually damaged [42]. According to Bettencourt et al. [27] many studies were expected to be done on the decreasing in mechanical properties because water molecules can act as plasticizers, altering the mechanical properties of the polymer. Moreover, Anusavice [43] stated that the polymer chains usually become more mobile and it can affect the mechanical properties. This finding is in agreement

with the one made by Nihei et al. [44] who reported that the mechanical properties of polymeric composite materials significantly depend upon the condition of the interface between surfaces of the inorganic filler particles and the polymerized organic resin in which the filler particles are embedded.
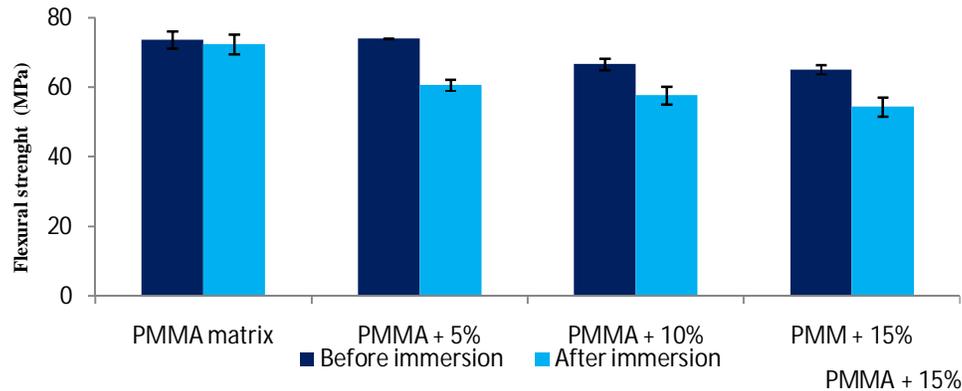

Figure 4: Effect of SBF exposure on flexural strength of PMMA matrix and PMMA α-cordierite composites compared to the same samples before exposure

Scanning Electron Microscopy

Figures 5 - 8 show the fracture surface of various formulations of denture base materials after 28 days of immersion in water and SBF. Figure 5 (a) (b) show (SEM) of the unfilled sample at 500 x and 1000 x magnification. At 500 x , it is clear to note that the absorption of samples led to build big cavities into PMMA matrix body. However, at 1000 x magnification, figure 5 (b) shows the penetration of water which made the surface seems like many layers into the PMMA matrix. This contributed to rapid crack growth and stable crack propagation. This resulted in a slightly lower flexural strength value in immersed pure PMMA samples compared to those exposed to air. Figure 6 (a) (b) shows the SEM of the fracture surface of α-cordierite 5wt % filled PMMA matrix at 500 x and 1000x magnification. At low magnification, as shown in figure 6 (a) the fracture surface seems to be rougher. This might be attributed to weak interaction between α-cordierite and PMMA matrix. This has affected in environmental properties. At high magnification, as shown in figure 6 (b) it can be clear see the filler particles aggregates which implicated in water absorption as they appear loosely embedded in the matrix. Hence, the water

can be faced the interface between these agglomerates and the matrix. Figure 7 (a) (b) shows the SEM of the fracture surface of α-cordierite 10 wt % filled PMMA matrix at 500 x and 1000x magnification. At a low magnification, as shown in figure 7 (a) the micro voids can be discerned clearly at this magnification. The presence of voids could be the strong cause to make

water paths which can lead to a lack of impregnation of filler particles with the polymer matrix [23]. At 1000 x magnification, figure 7 (b) displays the presences of cavities and cracks which can allow to water molecules come into the free spaces that cause progressively weakened.

Figure 8 (a) (b) shows that the SEM of the fracture surface of α-cordierite 15 wt% filled PMMA matrix taken at 500 x and 1000x magnification. At a low magnification, figure 8 (a), the fracture surface appears smooth and it is clear to see there are groups of filler particles are distributed equally beneath the surface of fracture and this helps the penetration of water. At high magnification, figure 8 (b) shows some micro-crack appeared and it is filled with the particles of filler thus, the water and SPF will take place into the crack area.
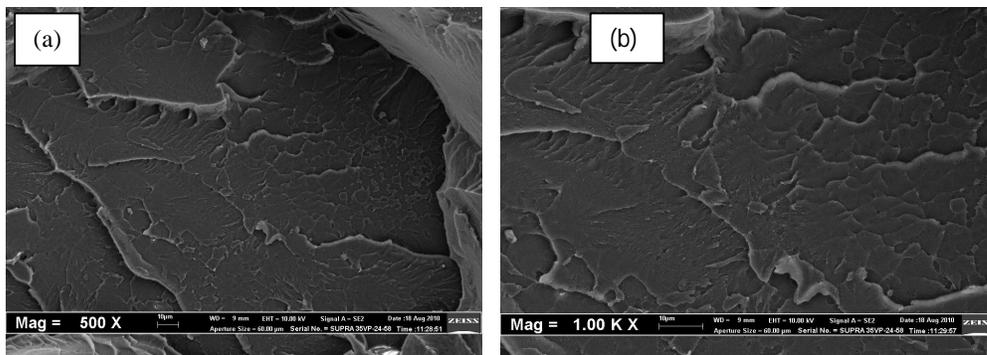

Figure 5: SEM micrograph of fracture surface of PMMA matrix after 28 immersion days at different magnifications. (a) 500x, (b) 1000x.
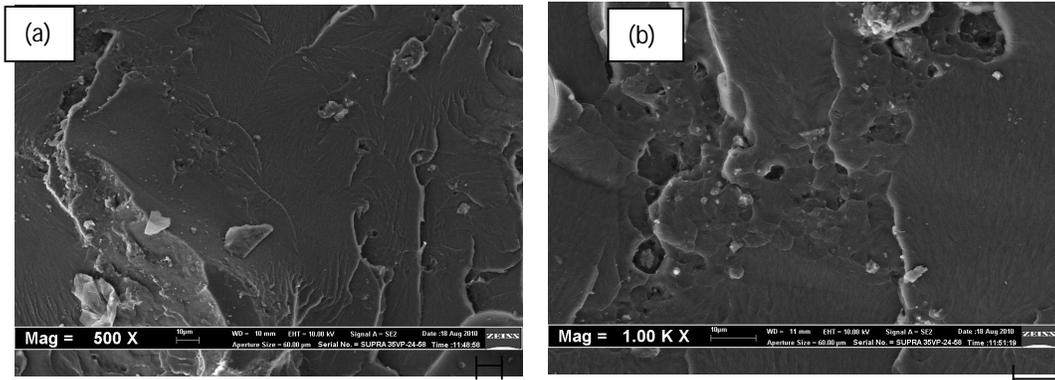
Figure 6: SEM micrograph of fracture surface of α-cordierite 5 wt% filled PMMA matrix after 28 immersion days at different magnifications (a)500x, (b) 1000x.
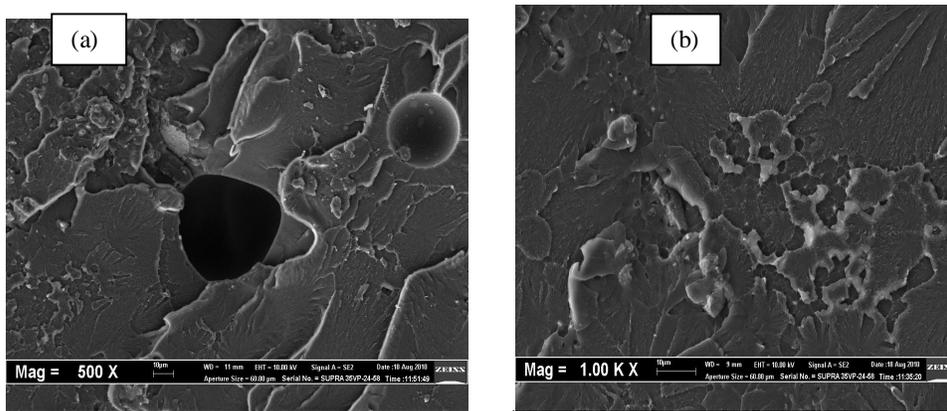

Figure 7: SEM micrograph of fracture surface of α-cordierite 10 wt% filled PMMA matrix after 28 immersion days at different magnifications.(a)500x ,(b) 1000x.

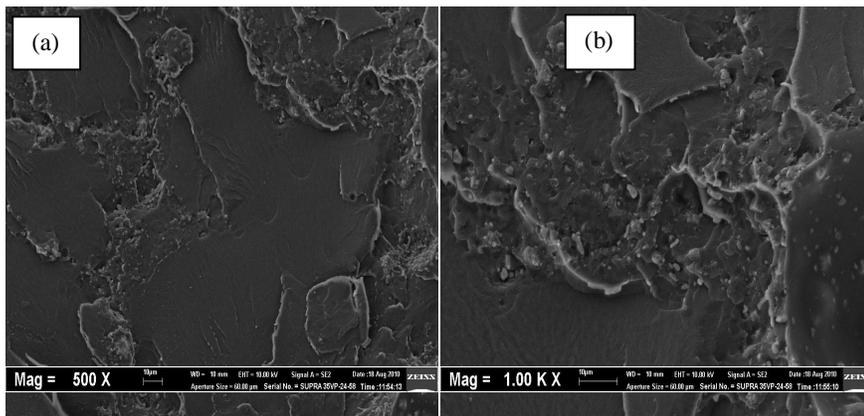

Figure 8: SEM micrograph of fracture surface of α-cordierite 15 wt% filled PMMA matrix after 28 immersion days at different magnifications. (a)500x, (b) 1000x.

Conclusions

The samples which continued with the treated filler showed higher water absorption compared to the unfilled samples. Also, the absorption of SPF was found to be more in the samples that contained treated filler. On the other hand, the solubility of SPF was less in the composites samples compared to PMMA matrix sample. Also, comparing between the PMMA matrix sample and the composites samples before immersion in water and SBF, the flexural properties in all samples were decreased after immersion.

Acknowledgments

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