Mechanical and Tribological Properties of PMMA-Sea Shell based Biocomposite for Dental application

R. Karthicka, P. Sirishab, M. Ravi Sankarc

Abstract

The material used for fabricating dentures should have good mechanical and tribological properties in order to withstand heavy forces inside the mouth. A study has been made to evaluate the hardness and tribological properties of the Poly (Methyl methacrylate) PMMA based denture composite reinforced with seashell nanopowder. The PMMA biocomposites containing 2%, 4%, 6%, 8%, 12%, 16% and 20% by weight of seashell nanopowder and an unfilled composite as control specimen were fabricated. The microhardness of the composites was found using Vickers hardness tester. The addition of 2% seashell nanopowder had no significant effect on the microhardness. But it was found that on increasing the seashell nanopowder content, the microhardness value increased till 12% and substantially decreased beyond 12% seashell nanopowder. The wear test was performed and frictional force generated during sliding of specimens were evaluated in pin on disc apparatus. The wear mechanism and dispersion of seashell nanopowder in the specimen were analyzed in Scanning Electron Microscopy (SEM). The wear resistant property increased on addition of seashell nanopowder with 12% seashell nanopowder reinforced composite showing least frictional force developed during the wear test. The 16% and 20% filled composite developed more frictional force than developed in 12% filled composite. It was concluded that PMMA biocomposite could be successfully reinforced by seashell nanopowder with better properties at 12% seashell nanopowder content followed by 8% filled composite.

Keywords: PMMA biocomposite; Methyl methacrylate; seashell nanopowder; wear;
1. Introduction:

The two materials which do not dissolve in each other and together produce a composite material of unique properties. Generally one of the materials, reinforcing filler materials such as fibers, particles are added to the continuous phase material in order to enhance the composite properties. The main function of the filler is to increase the mechanical properties by reinforcing the continuous matrix and providing appropriate degree of translucency and lower shrinkage properties. T. Kanie et al. (1999) stated that one of the methods to improve the mechanical properties of the composite is by adding the filler material in the continuous phase. The mechanism of toughening is due to the matrix-filler interactions leading to improved mechanical properties (Dental restorative materials, Craig). Robert J. Kane et al. (2010) studied the reinforcement effect of acrylic bone cements with the addition of zirconia fibers. They found that the addition of 15% and 20% zirconia fibers increased the fatigue life.

The composites where the filler material is embedded into an organic polymer resin are called polymer composites. The particulate composites are composites with particles as reinforcing filler material such as silica, quartz, glass called particle reinforced composite. The composite materials comprising of one or more phases derived from a biological origin are called biocomposites. The distinct constituent phases used in composite should be compatible with the biological environment and the interface between the distinct phases should not be affected by the body environment. In biocomposites, the problems of corrosion and release of allergenic metal ions, such as nickel or chromium are eliminated. Biopolymer resin composites are widely used for the direct restoration of both anterior and posterior teeth, because of the aesthetic, physical and mechanical properties of those materials (Evangelia C. Vouvoudi et al. (2012)). Biocomposites are light weight and are used for dental post, hard tissue applications, prosthetic socket, external fixator, bone plate, orthodontic archwire, orthodontic bracket, total hip replacement.

In dentistry, one of the predominantly used polymers is Poly (Methyl methacrylate)-PMMA (Farideh Bahrani et al. (2012); Kuhar M and Funduk N (2005); Mese (2007)). It is widely used for fabricating dentures. A denture is a removable replacement for missing teeth and surrounding tissues. The important property of such a denture is it should be compatible with the body environment. It must have good wear and mechanical properties so that it could withstand heavy chewing forces and wear developed inside the mouth. The biocompatibility and excellent aesthetic appearance of PMMA makes it suitable for fabricating dentures. It has got lower water sorption capability and relative lack of toxicity (Farideh Bahrani et al. (2012)). Although it is widely used, there are many drawbacks while considering the wear and mechanical properties of the PMMA which leads to early crack and fracture in clinical use (Robert J. Kane et al. (2010); T. Kanie (1999); Tomohiro Kawaguchi et al. (2011)). The mechanical and tribological properties of PMMA are of primary concern in fabricating dentures. T. Kanie (1999); Klaus D. Jandt and Bernd W. Sigusch (2009) studies reveal that the hardness and wear are the major issues of PMMA denture.

The Tribological property depends on both the material and the condition under which the material is used. Wear in general is a consequence of the interaction between surfaces moving in contact, causing gradual removal of material. Low wear resistance is one of the major reasons for their limited acceptance in crucial applications (Wei Ping Wang et al. (1998)). And since the denture is subjected to heavy wear during their life time, the study of wear behavior of the denture was considered important. The resistance of composite resin to wear depends on the nature of the filler added (Dental Restorative Materials, Craig).

Ross Ormsby et al. (2010) incorporated 0.1 weight% multiwalled carbon nanotubes (MWCNT) to PMMA bone cement. They found that the mechanical and thermal properties of the composite were enhanced by the extent that depends on type of MWCNT. They claimed the reason for achieved better properties to be uniform dispersion of MWCNT within the PMMA cement.

Farideh Bahrani et al. (2012) compared the microhardness and surface roughness of two denture base materials Meliodent (Acrylic heat polymerized resin) and FuturaGen (Acrylic self-polymerized resin). They found that self-polymerized resin FuturaGen showed slight increase in microhardness (21.48, 1.42HV) and roughness (0.84μm) than heat polymerized resin.

Moszner N and Klappdor S. (2004) claimed that nanocomposites have improved better compressive strength, diametrical tensile strength, fracture resistance, wear resistance, low polymerization shrinkage, high translucency, high polish retention and better esthetics.
Seashell is one of the natural materials which is not used in dental applications. Seashells are natural ceramics similar to our teeth and bones. Natural ceramic seashells have pearly layers, also known as nacreous layers. They are arranged in layers of calcium carbonate platelets and protein. It consists of more 30 proteins that are held together to provide more strength and toughness. J. González et al. (2005) studied the comparison of seashell reinforced polypropylene (PP) and seashell reinforced High Density Polyethylene (HDPE). They found that the incorporation of seashell increased the Young’s modulus. In Dentistry, although many studies have improved the mechanical properties, still there are many problems with mechanical and tribological properties of dentures.

The aim of the present paper is to fabricate PMMA based denture biocomposites reinforced with nanosized seashell powder and to study the effect of seashell nanopowder on microhardness and wear property of the composites.

2. Materials:

2.1. Poly (Methyl methacrylate) based denture resin:

Acrylic denture resin, Surgical Simplex P is received from Stryker® Howmedica. It has two components. One component is an ampoule containing monomer liquid, which is colourless, flammable and has sweet acrid odour.

The monomer liquid contains:
- Methyl Methacrylate
- Hydroquinone
- N, N-dimethyl para toluidine (NDPT)

Methyl methacrylate is an unpolymerized monomer of density 0.94g/cm³. N, N-Dimethyl para toluidine (NDPT) causes decomposition of Benzoyl Peroxide (BPO) and this releases free radicals to initiate polymerization. Hydroquinone is present as an inhibitor which prevents polymerization reaction when exposed to light or elevated temperatures.

The other component is a packet which contains:
- Poly (Methyl methacrylate)
- Methyl methacrylate
- Barium Sulphate

Poly (Methyl methacrylate) is a polymer of density 1.18g/cm³. Methyl methacrylate is added as a styrene copolymer which contains 1.7% Benzoyl peroxide as initiator. Barium Sulphate is added as a Radiopacifier.

3. Experimentation:

3.1. Preparation of seashell nanopowder and seashell nanopowder reinforced composite:

The seashell biomaterial was initially grounded to smaller particles by hammering and then transferred to mono chamber ball-mill machine. Zirconia ball (Mohs hardness-7) was used to mill the smaller seashell particles (Mohs hardness-3.5) to a fine powder. The ratio of weight of Zirconia balls to seashell particles was 10:1. 9 zirconia balls (30g) were taken to mill 3g of seashell particles. The rotational speed was set to 200RPM and duration of ball milling was 1 hour. For every one hour, the balls were removed. It was well cleaned with ultrasonic bath since the powder stuck around the surface of the balls should not be a hindrance to the next 3g of seashell particles. The experiment was repeated until very a fine seashell powder of less than few nanometers was achieved. The obtained nanopowder was then dried for 3 hours in order to remove the moisture. Figure1 shows the preparation of seashell nanopowder from seashells.

The required quantity of PMMA powder and seashell nanopowder were taken in the mono chamber ball mill machine with weight percentage as shown in Table 1. It was mixed until the seashell nanopowder was uniformly distributed in the PMMA powder. The mixed powder was then transferred to a well cleaned empty beaker. The
corresponding weight percentage of MMA liquid (Table 1) was poured into the beaker containing uniformly mixed PMMA powder and seashell nanopowder. The PMMA powder to MMA liquid ratio was added in a ratio of 2:1 along with seashell nanopowder and the room temperature was maintained at 25°C. It was mixed well with the stirrer until wetting of all powder particles is done. This initiates free radical polymerization and it was poured into the mold of required dimension needed for testing the specimen according to corresponding ASTM standard. The separating medium was used in order to separate resin and mold and for easy removal of the specimen. It was left for few minutes until it is hardened. Finally, a hard seashell nanopowder reinforced composite was removed from the mold. In a similar way, all the specimens were prepared with weight percentage of seashell nanopowder, PMMA powder and MMA liquid as shown in Table 1.

Table 1. Composition of different seashell nanopowder reinforced composites.

<table>
<thead>
<tr>
<th>Weight percentage of Seashell nanopowder (%)</th>
<th>Weight percentage of PMMA powder</th>
<th>Weight percentage of MMA Liquid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>66.67</td>
<td>33.33</td>
</tr>
<tr>
<td>2</td>
<td>65.33</td>
<td>32.67</td>
</tr>
<tr>
<td>4</td>
<td>64.00</td>
<td>32.00</td>
</tr>
<tr>
<td>6</td>
<td>62.67</td>
<td>31.33</td>
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<tr>
<td>8</td>
<td>61.33</td>
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<tr>
<td>12</td>
<td>58.67</td>
<td>29.33</td>
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<tr>
<td>16</td>
<td>56.00</td>
<td>28.00</td>
</tr>
<tr>
<td>20</td>
<td>53.33</td>
<td>26.67</td>
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</tbody>
</table>

When MMA liquid is added to the PMMA powder, it undergoes chemical activation. The N, N-Dimethyl para toluidine (NDPT) present in the liquid causes decomposition of Benzoyl peroxide. This releases free radicals containing unpaired electron (Figure 2). This unpaired electron gets paired with carbon atom on reacting with one unit of Methyl methacrylate. This on further reaction with many units of methyl methacrylate, continuous chain of repeating units is formed by polymerization growth followed by chain termination to produce Poly (Methyl methacrylate).
3.2 Microhardness:

The prepared specimens were checked for microhardness under Vickers microhardness Tester (Figure 3: Vickers microhardness Tester, BUEHLER, USA). A diamond pyramid with the square base and an angle of $136^\circ \pm 0.5$ between the opposite faces was used as an indentor. A force of 100kgf was applied at the surface of the specimen. A diamond shaped indent formed was seen under microscope and the diagonals of the diamond shaped indent was measured to find the Vickers hardness ($HV$) based on the formula:

$$HV = \frac{2F \sin \frac{136^\circ}{2}}{d^2}$$

$$HV \approx 1.854 \frac{F}{d^2}$$

$F$ represents load in Kgf

d represents arithmetic mean of the two diagonals (mm)

$HV$ represents Vickers hardness

A force of 100Kgf was maintained constant for all specimens and ten readings were taken for each specimen. The average of the values represent the hardness values of the each specimen.
3.3 Statistical Analysis:

The average hardness values of all the specimens were collected. Data obtained were analyzed by One-way analysis of variance (ANOVA) to interpret the result. The null hypothesis was that the addition of seashell powder has no effect on the microhardness of seashell reinforced PMMA composite. The alternate hypothesis was that there are changes observed on the microhardness of the composite with the addition of seashell nanopowder. The differences were significant at the level of P<0.05.

3.4 Wear:

The prepared specimens were polished using 600 grit sand paper in the Grinding machine. The specimen followed ASTM standard G99-05. In wear tests, the specimens were made to slide against the stainless steel disc counterpart of hardness 954 HV with diameter of 100 mm and thickness of 6 mm. Diameter of the wear track was 50mm. After the specimen was mounted, lever arm was mounted by counter weights of 15N. Wear experiment was performed for 15 minutes at a rotational speed of 40RPM. (Figure 4: Pin on Disk apparatus, Ducom Instruments, Bangalore, India). The diameter of the wear track, counter weight, duration of experiment, rotational speed were maintained constant for all specimens and wear of each specimen was found in digital display.
4. Results and Discussion:

4.1. Microhardness:

The average Vickers hardness (HV) of the specimens are shown graphically in Figure 5. It was found that the addition of seashell nanopowder showed increased microhardness. The One-way ANAVO confirmed that the addition of seashell nanopowder made significant changes in the microhardness values of PMMA composite. But initially there was no statistically significant difference by adding 2% seashell nanopowder (P>0.05). Significant increase was achieved by adding 4% seashell nanopowder (19.83HV) but the presence of 12% seashell nanopowder showed maximum microhardness (25.12HV) which is more significant than that of 4% filled composite. No significant difference was observed between 4% (19.83), 6% (20.02HV) and 8% (20.93HV) filled composite (P>0.05) although there was a slight increase in microhardness. Addition of seashell nanopowder beyond 12% seashell nanopowder showed significant decrease in microhardness which could be clearly understood from figure 5 (P<0.05).

![Figure 5: Effect of addition of seashell nanopowder on microhardness values of the composites](image)

SEM observation at same magnification of 4% and 12% seashell nanopowder reinforced composite which showed significant variation in microhardness values are presented in Figures 6a and 6b. The difference in the intensity of seashell nanopowder between 4% and 12% seashell reinforced composite could be clearly seen from the figures. The 4% seashell reinforced composite (Figure 6a) had lesser amount of seashell nanopowder around the composite and hence the interaction between the seashell nanopowder and the resin was limited. Ultimately, the reinforcement of the 4% seashell nanopowder composite was also weaker when compared to that of 12% seashell nanopowder composite. On the other hand, 12% seashell nanopowder composite (Figure 6b) had more amount of seashell nanopowder content and better interaction of seashell nanopowder to resin was occurred. Also almost uniform dispersion of 12% seashell nanopowder provided enough space between the seashell particles which increased the reinforcement of the bio-composite and increase in microhardness value of the bio-composite was occurred. This satisfies with the study of Ross Ormsby et al., 2010, which stated uniform dispersion can increase the mechanical properties of the PMMA composite.

The Figure 6c shows scanning electron micrograph of 20% seashell nanopowder composite in which the addition of more seashell nanopowder beyond 12% has reduced the space between the seashell particles due to high intensity of seashell nanopowder resulting in non-uniform dispersion and agglomeration of filler particles at some places. Hence at those places the interaction between the seashell particles exceeded the interaction between seashell filler and resin. The Figure 6c shows comparatively larger size and more intensity of seashell particles of 20% seashell nanopowder reinforced composite than that of 4% and 12% seashell nanopowder reinforced composite (Figure 6a
and 6b). Hence it showed significant reduction in microhardness of 20% filled composite compared to that of 4% and 12% filled composite.

![Fig.6: Scanning electron micrographs of various amounts of seashell nanoparticles in PMMA composite material (a) 4%, (b) 12% and (c) 20%](image)

The uniform dispersion of seashell nanopowder at its optimum content of 12% (Figure 6b) might have enhanced due to proper mixing of powder in the Ball-mill machine. Ball milling of the PMMA powder and seashell nanopowder might have led to better distribution of seashell particles and hence improvement in microhardness would have occurred.

Xinjing ZHANG et al, 2012 evaluated the mechanical properties of Poly (Methyl methacrylate) reinforced with unmodified and silanised Aluminium borate whiskers (ABW). They found the Vickers microhardness values of both unmodified and modified Aluminium borate whiskers reinforced composite. The Vickers microhardness values of 5%, 10%, 15%, 20% unmodified Aluminium borate whiskers were 18.70HV, 18.37HV, 21.23HV, 20.15HV, which agreed with the microhardness values of 4%, 8%, 12%, 16% seashell reinforced PMMA composite (19.83HV, 20.93HV, 25.12HV, 18.96HV). In their study, the maximum microhardness values obtained was 23.15HV for 15% silanised Aluminium borate whiskers. It was observed that 12% seashell reinforced composite which had maximum microhardness of 25.12HV in this study was slightly higher than that of 15% modified ABW reinforced composite.

The occurrence of porosity may be due the evaporation of monomer when the temperature of the resin increases during curing of the composite. The 20% seashell nanopowder composite had more micropores, which was also responsible for the decrease in microhardness of the composite. Figure 7a shows scanning electron micrograph of micropores in the surface of 20% seashell composite which was occurred when the curing process was taking place. Figure 7b shows the presence of filler particles inside the micropores.

![Fig.7: Scanning electron micrograph of 20% seashell nanopowder reinforced composite (a) Presence of micropores, (b) Presence of seashell inside the micropore.](image)

When PMMA powder and MMA liquid are mixed in the ratio 2:1, NDPT causes decomposition of Benzoyl peroxide. The Benzoyl peroxide present as initiator, initiates the free radical polymerization of MMA monomer to form PMMA polymer. The degree of conversion describes the extent of polymerization of MMA monomer to PMMA polymer. The degree of conversion depends on the composition of the material and the condition of curing. The degree of conversion of the composite was indirectly measured by measuring their hardness values. The
difference in hardness of the composite might be due to difference in degree of conversion with different seashell nanopowder composition. The degree of conversion also affects the mechanical properties of the composite (Dental Restorative Materials, Craig). The PMMA composite specimen with 12% seashell nanopowder might have had more degree of conversion than that of other specimens, which might be the root cause of more microhardness of material than other material. So, composite with 12% seashell nanopowder might have increased the degree of conversion and hence the leakage of monomer would also be lesser than other composite specimens. The leakage of less monomer content also reduces the toxicity issues in the oral environment. During polymerization of MMA monomer, some monomer still remain unreacted in the polymer resin. This unreacted residual monomer affects the mechanical properties of the composite. The increase in microhardness of 12% seashell composite might also due to the presence more unreacted monomer in the polymerized resin, which undergoes further polymerization at the active sites. The residual monomer content might have increased by adding the seashell nanopowder up to 12%. Further addition of seashell nanopowder might have decreased the residual monomer, so decrease in hardness values was obtained. In order to validate the effect of residual monomer on the microhardness, further study is recommended for the seashell reinforced composites.

4.2. Wear:

Figure 8 shows the frictional force of different compositions of seashell nanopowder reinforced composites versus duration of sliding against the steel disc counterpart. It was observed that the unfilled composite started initially with 6.75N and it steadily increased up to 7.80N over within 200 seconds and after that it remained constant for the rest of the experiment. The similar trends of curves were obtained for all other composites with different constant frictional force values after steady increase. From the graph, the unfilled composite had maximum frictional force at the contact surface and 12% seashell filled composite had least frictional force followed by 8% filled composite. The initial low frictional force for the curves may be due to deposition of foreign material on the surface of the disc due to exposure to atmosphere, which acts as a lubricating layer. But once the lubricating layer was removed off, true contact of composite with the steel disc occurred. During sliding of the composite material and steel disc counterpart, the debris were developed at the contact surface due to the heavy plastic deformation of thin surface layer and debris were removed off from the contact surface. Some of the debris was stuck between the two surfaces. Due to the inclusion of such trapped debris, the frictional force of the composite increased. After a period of time, no more removal of debris was occurred and frictional force at the contact surface was constant for the rest of the experiment.
During sliding of the two surfaces, the ploughing effect of the nanopowder particles was occurred. The repeated ploughing of the nanopowder particles at the sliding surface produced high dislocation densities and due to which the microstructure of the composite material was affected. The change in microstructure is based on the condition the experiment was carried out. The speed and heat generated at the interface affects the microstructure of the composite. Figure 9 shows the dislocated particles due to ploughing action during the wear tests of 4% filled composite.

![Ploughing of seashell nanopowder](image)

**Fig.9.** Field emission scanning electron micrograph of 4% seashell nanopowder filled composite

The scanning electron micrograph of wear patterns of 8% and 12% seashell nanopowder, which had lesser frictional force of all the composite is shown in the figure 10. The arrow mark indicates the direction of wear track. There was no significant change observed in the wear tracks of 8% and 12% filled composite as supported by the figure 8, where the frictional force curve of 8% filled composite was closer to 12% filled composite than other composites.

![Scanning electron micrograph of wear tracks of biocomposites containing a) 8% seashell nanopowder; b) 12% seashell nanopowder](image)

**Fig.10.** Scanning electron micrograph of wear tracks of biocomposites containing a) 8% seashell nanopowder; b) 12% seashell nanopowder

The decrease in the frictional force of 2% filled composite from 100 to 150 seconds was not desirable. This decrease in the frictional force may be due to the change in shear rate which affects the mechanical properties of the composite.

Wear behavior and frictional force were analyzed thoroughly with respect to size of the filler, their dispersion and composition in the composite. The PMMA biocomposites with 0%, 2%, 4%, 6% seashell percentages had less amount of seashell nanopowder content to uniformly disperse in the resin. So they tend to form groups of very fine powder to form bigger size seashell particles. The agglomeration of the particles was reduced significantly by increasing the seashell nanopowder content to 12%. This might be due to the increase in the amount of seashell nanopowder which caused break down of the seashell nanopowder agglomerates by rubbing against one another during mixing. Addition of seashell nanopowder beyond 12% increased the seashell-seashell interaction which again led to formation of agglomeration. So, the 12% seashell reinforced PMMA composite had optimum dispersion in the matrix with very less agglomeration. Hence it had enough spacing between the seashell particles such that the good bonding and reinforcement of the seashell particles to resin was achieved, which still enhanced the wear resistance property. As already seen from the figure 8, there was no significant change observed between 8% and 12% seashell nanopowder reinforced composite. Since there was less agglomeration seen in 12% seashell reinforced composite, the particles were situated very closely and the matrix surface was protected from wear. This might also be the
reason for less wear in 12% seashell nanopowder reinforced composite. The 16% filled composite had larger agglomerated particles, which is formed due to addition of more seashell nanopowder. The repulsive force between the particles was less compared to that of 12% seashell reinforced composite, hence the agglomeration of particles in 16% seashell nanopowder was seen. The figure 11 shows the agglomerated particles of seashell nanopowder in 16% filled composite.

Since the size of agglomerated particles in more seashell nanopowder reinforced composite was larger, more easily the filler particles got dislodged from its position, which led to more wear of the composite. Also, due to the presence of larger and harder particles in 16% and 20% filled composite, the microcrack and void formations were developed during the plastic flow of material during the wear tests. The figure 12 shows the formation of voids around the large filler agglomerates in the worn track of 16% filled composites.

5. Conclusion

The addition of 2% seashell nanopowder slightly increased the microhardness values. The significant change in the microhardness was seen when the seashell nanopowder content increased to 4% and maximum microhardness was achieved by adding 12% seashell nanopowder. In 12% filled composite, uniform dispersion, better filler matrix interactions and reduced porosity are the primary reasons for maximum microhardness. Further addition of seashell nanopowder resulted in decrease of microhardness due to high intensity of seashell nanopowder which affected the morphology of the composite and increased the porosity of the composites.

The increased wear property due to addition of seashell nanopowder was indicated by drop in the frictional force generated at the contact surface. The frictional force was dropped till the seashell nanopowder content reaches its optimum content of 12%. The uniform dispersion and stronger reinforcement in 12% filled composite was responsible for better wear property. Of all the composites 12% and 8% showed better wear resistant property. Increasing the seashell nanopowder content beyond 12% favored agglomeration and affected the morphology of the
composites due to which more stress was developed at the interface. This led to poor bonding of the filler particles and got dislodged from its surface. The ploughed and removed filler particles trapped between the surfaces resulted in generation of more frictional force at the contact surface while sliding against the steel disc counterpart. Hence the PMMA could be successfully reinforced by seashell nanopowder with optimum properties at 12% seashell nanopowder followed by 8% seashell nanopowder.

References


