Hardness optimization of epoxy filled PTFE with/without 
TiO$_2$ filler

Nur Hidayah Ibrahim, Dr. Ahmad Zafir Romli and Dr Nik Noor Idayu Nik Ibrahim

Faculty of Applied Sciences, Universiti Teknolgi MARA, 40450 Shah Alam, Selangor, Malaysia, Centre of Polymer Composite Research and Technology (PoCResT), Institute of Science, Universiti Teknologi MARA Shah Alam, Selangor, Malaysia

Abstract. Osteoporosis is one of the bone diseases that have the highest number of patients. Throughout the years, there are multiple choices of material that has been used for bone implant such as metals or plastics. The uses of these materials in medical implant are not permanent and they needed to be changed because of its low hardness that would cause pain. In this paper, a new micro bearing concept system by using polymer composite was introduced where epoxy was used as the matrix to improve hardness of micro filler and this composite later can be used in medical implant. PTFE powder filler was used and incorporated at 1%, 3%, 5%, 7% and 10% in the epoxy system respectively. Acetone was used as diluents in the epoxy to improve filler dispersion. Another set of epoxy filled PTFE at 1%, 3%, 5%, 7% and 10% was added with 2% of titanium oxide (TiO$_2$) and results were compared in terms of hardness and density. Result showed composite with TiO$_2$ incorporation obtained highest values which were 5% increase at 3%PTFE loading and 1% increase at 10%PTFE loading for hardness and density respectively compared to the composite without TiO$_2$.

1. Introduction

Hardness is one of the most important factors when it comes to medical implant so that it helps to prolong the life of the implant itself. Problem would arise when the material used for medical implant such as ultrahigh molecular weight polyethylene (UHMWPE), polymethylmetacrylate (PMMA), polyethyetherketones (PEEK), and polytetrafluoroethylene (PTFE) has low hardness [1]. Problem such as osteolysis will arise when the materials have low hardness. Osteolysis is the process where the tissue around the implant is disappearing caused by the articulating surface. The movement of this implant will result in the formation of debris when the materials are soft. Therefore, the implant will not function well and cause pain to the patients [2]. The use of UHMWPE gives excellence result for total joint arthroplasties in long term and PTFE on the other hand has been used as solid lubricant bearing implant in knee implant. PTFE has outstanding properties for this application as it has superior wear resistance. Apart from superior wear resistance, it also gives high fracture toughness. These properties made PTFE to be used broadly in many applications substituting many other materials. PTFE has a very low coefficient when it is rubbed between against two metallic surfaces making it suitable for bearing application [3]. It has lower friction coefficient compared to other engineering materials such as nylon, high density polyethylene (HDPE), low density polyethylene (LDPE), and polyetherethketone (PEEK). However, the uses of these materials in medical implant are not
permanent and they needed to be changed over the years. These materials have low hardness leading to possibility to fractured or dented causing pain to patient.

In this study, PTFE will be used as filler into the epoxy. In some studies, it is proved that adding PTFE filler can potentially enhance wear of epoxy while improving the PTFE hardness. Good mechanical strength and hardness, as well as thermal and chemical resistance, helps the application of epoxy resins as commercially used engineering materials. The behaviour of epoxy material in terms of wear and friction will be improved when the adhesion to the counterpart material is reduced while enhancing its hardness and stiffness. This can be achieved by adding PTFE as filler into epoxy systems [4]. In other studies, the performance of epoxy is modified by adding different fillers. Researchers have found that adding fillers such as alumina (Al2O3) and boron carbide (B4C) will improve mechanical properties of epoxy. As to reduce the friction and the wear environment of epoxy, solid lubricants such as graphite, PTFE and molybdenum sulphide are used [5], [6]. For the last decade, fillers such as carbon fibre and graphite have been widely used to improve the mechanical properties of PTFE [7].

This study produced a solid lubricant micro bearing polymer composite based on the epoxy system as the construction material in which later can be substitute for the plastic bearing in medical implant. Polytetrafluoroethylene (PTFE) was incorporated in the epoxy system. On the other hand, Titanium dioxide was also added into other set of formulations as wear resistance filler and result showed those composite with TiO$_2$ filler have improved hardness.

2. Experimental details

2.1. Materials and manufacturing

2.1.1. Polytetrafluoroethylene powder.
PTFE powder obtained was supplied from GoodFellow Cambridge Limited Huntington PE29 6WR England. It was manufactured from Sigma-Aldrich GF20091743-1EA United Kingdom. The average particle size of the powder was 20 micron. Apart from average particle size, its density was 2.2 g/cm$^3$. PTFE is non polar material thus it does not dissolve in water or any polar solvent. The powder came in irregular shape and in a large agglomerate size (several hundred microns) rather than fine powders. This condition made it hard to incorporate PTFE into the composite [8]. That led to the need of reducing the size of the clump powder prior to mixing stage. Hence, PTFE powder was blended using steel blender to obtain fine powder. The PTFE powder was then sieved using 360 mesh sieves.

2.1.2. Epoxy and hardener.
The epoxy and hardener (amine) used in this experiment was supplied from Vistec Technology Services and manufactured from Oriental Option SDN BHD. This epoxy and hardener were EPOXEN CP362 part A and EPOXEN CP362 part B type resin and hardener. It has transparent colour and provides glossy hard surface after fully cured. The viscosity of epoxy and hardener were 7000 MPa.s and 300 MPa.s respectively. The mixing ratio for epoxy and hardener was 100 to 50 parts by weight. It took 3 hours to cure and 10 hours to fully cure. Cured epoxy has hardness of 90D and water absorption <0.5%.

2.1.3. Titanium dioxide (TiO$_2$).
TiO$_2$ powder (224227) used was manufactured from SIGMA-ALDRICH 3050 Spruce Street, Saint Louis, MO 63103, USA. It came in powder in white colored. The average particle size of TiO$_2$ was $\leq$ 5.0 micron. The density of TiO$_2$ powder was 4.23 g/cm$^3$. Before TiO$_2$ powder was used, it was also sieved using 360 mesh sieves because some of the powders were also agglomerated. It was used as a filler to enhance the wear properties of the micro-bearing composite.
2.1.4. Acetone.
Acetone (C₃H₆O) used was manufactured from Classic Chemicals SDN BHD Temasya Industrial Park, 40150 Shah Alam, Selangor Darul Ehsan, Malaysia. The appearance was clear and bright. The density of the acetone was 0.792 g/cm³. It was used to reduce the viscosity of the epoxy as well as to ease dispersing of the filler while mixing.

2.1.5. Methodology.
In this paper, PTFE was used as the filler to be incorporated in the epoxy where epoxy acts as matrix. Instead of obtaining homogenous mixture, PTFE on the other hand should sink forming a layer at the bottom of the composite due to PTFE having greater density compared to epoxy. So instead of floating to the surface it sunk in the bottom. According to different addition quantity, two groups of samples having 1%, 3%, 5%, 7% and 10% of PTFE loading have been prepared for each group. One group of the sample is added with constant amount of TiO₂ at 2% loading.

![Method flow chart]

Figure 1. Method flow chart

3. Result and discussion

3.1. Effect of TiO₂ filler on PTFE filled epoxy
Figure 2 and 3 below shows the density and hardness result of the composite. The density test was carried out on specimens by taking 3 samples on average. Density test was done using the Densimeter (g/cm³). It can be seen on the graphical representing on the figure 2a, the density of the composite was increased with the increased amount of PTFE loading. The increasing filler content increase the volume fractions thus increasing the density value. The properties of composites were significantly influenced by the density property [9].
Figure 2. (a) Density without TiO$_2$ (b) Hardness with TiO$_2$

The hardness result in figure 3a also showed an increasing trend in the graph. This stated that the hardness of the composites in figure 3a increased as the density in figure 2a increased. There was only 1.4% increase in density for 3% PTFE loading with TiO$_2$ in figure 2b compared to 3% PTFE loading without TiO$_2$ filler in filler compared figure 2a. The fluctuation of result can be seen in figure 2b. The main reasons for this are the ceramic powders tend to agglomerate causes bad dispersion in the PTFE matrix which produces more pores in the matrix. It is more difficult for PTFE to have a good adhesion with TiO$_2$ fillers so that many pores appeared which results in the decline of density. It is difficult for PTFE to have strong adhesion with ceramic powder as PTFE has a low surface energy for 5% and 7% loading fillers as can be seen on figure 2b.

Figure 3. (a) Hardness without TiO$_2$ (b) Hardness with TiO$_2$

The hardness test was carried out on specimens by taking 3 sampling points. Hardness test was done using the Rockwell method with an R scale (HRR) which has no unit. The graphical representation of figure 3a showed that the hardness of the composite was slightly increased. The 3% PTFE content was increased at 11.7% than the 1%PTFE loading content followed by the increase of 5% PTFE and 7% PTFE load content at 0.6% and 1.3% respectively when the amount of PTFE filler was added. However, the result showed decreasing at 9.7% in hardness at 10% PTFE loading. Factors such as filler size and shape can greatly affect the hardness of composite [10]. This could be explained when the point where the particles are in contact with the matrix is reached as the result of the increasing of volume-fraction filler. After this point, stress is transferred across the material mostly via (hard) particle-particle interactions [4][10]. This showed the non-linear dependence of modulus, hardness and related properties with filler content, as seen in figure 3a for 1% PTFE to 7% PTFE loading. Hardness is also influenced by the specific composition and structure of the organic matrix.
This effect is enhanced for certain monomers, but has also been shown to be enhanced in composites with less filler concentration which might be the cause of reduction in hardness value for 10% PTFE loading. As for the graphical representing on figure 3b, it can be seen that the value of hardness generally was higher when 2% of TiO$_2$ was added in all PTFE loading epoxy composites. The highest hardness could be seen at 3%PTFE loading with TiO$_2$ incorporation which was 5% higher than the hardness without TiO$_2$ incorporation. However the decreasing in obtaining the result for composites with added TiO$_2$ filler at 5% and 7% might be due to problem in term of filler to filler interaction between PTFE and TiO$_2$ as well as the interaction between filler to matrix of both these two fillers with the epoxy system as discussed at the density section where the ceramic powder tend to agglomerate and PTFE fillers on the other hand has low surface energy causing these particles to have poor adhesion thus producing pores within the matrix making it less compact and decreasing its density as well as hardness value. However, we could see an increase for 10%, this might be due to PTFE filler has become dominant thus contributing in its higher density as well as hardness.

4. Conclusion

The results of testing observations provide few conclusions: the largest value of density, 2%PTFE with TiO$_2$ incorporation which was 1.4% higher than the composite without TiO$_2$. The largest hardness value, which was 3%PTFE loading with TiO$_2$ which was 5% higher than the composite without TiO$_2$. In conclusion, the TiO$_2$ filler incorporation increased the density and hardness of the composite.

5. References

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