Optimization of wear characteristics of PLA material reinforced with HAP nanoparticle by using taguchi technique

Sumit R Agrawal and Sali R Kulkarni
Department of Mechanical Engineering, GEC, Aurangabad, India
Email. sumit.agrw1992@gmail.com

Abstract. In the field of biomedical application, the polymer composite has been played a very challenging role and its used has been increasing since it possess good tribological properties when reinforce with appropriate material. In this regard, PLA (poly lactic acid) and its composite with HAP (Hydroxyapatite) was studied for its tribological behaviour which may be used as an implant material. PLA with varying percentage of HAP nanoparticles was examined on linear reciprocating tribometer under dry sliding test for specific wear rate. Design of experiment was based on Taguchi technique for optimizing specific wear rate parameter. In this study, effect of reinforcement and operating parameters that is load and frequency on tribological performance of PLA Nano composite was studied. ANOVA (Analysis of Variance) has been used to determine the influence of each parameter on wear characteristics. Regression analysis was used to establish a regression equation between all affecting parameters. The results shows that reinforcement plays a major role while load and frequency plays an average role on wear characteristic of PLA Nano composite. It was observed that PLA reinforced with HAP nanoparticle significantly improve wear characteristic up to 5% of reinforcement while beyond it, there is reverse nature of composite. The optimum parameter for wear rate were 5% reinforcement of HAP, 80 N of load, and 7 Hz frequency.

Keywords. PLA, HAP, Taguchi technique, Wear, ANOVA, nanoparticles

1. Introduction
In past decades, it has been seen that the researchers has shift from metal to its alloy and then ceramics and their composite, to achieve combine effect of both material into single. With the evolution of composite material, it is possible to achieve light weight with high strength of material which improves the efficiency as well as reduces the cost incurred in product life cycle. Now a days, the composite is one of the focused area of most of the researchers trying to find more and more reliable material.

Now the recent trend is on polymer and its composite. Basically polymer is lighter in weight as compare to other material and also possess good strength which can be enhanced to greater extent by reinforcing other element like ceramics and fibrous material. Polymer also proven its wide area of application in biomedical field, automobile, aircraft etc. replacing other material due to its good compatibility and ease of manufacturing. Mainly for biomedical application of polymer, lot of study is going on, since it has been seen that some previously used implant has some drawbacks as shown in detail in following table no. 1 which lowers the life of implant.

Various polymer like HDPE (High density polyethylene), UHMWPE (ultrahigh molecular weight polyethylene), PEEK (Poly ether ether ketone), PTFE (Poly tetra fluoro ethylene) etc. shows improvement in the wear property when reinforced with ceramics like Al₂O₃, TiO₂, Carbon fibre(CF), Kevlar fibre, SiO₂ etc. The reinforcement of HDPE with Kevlar fibre at 10% shows optimum results in
term of wear rate and biocompatibility also enhanced with increase in percentage of Carbon fibre [1]. The UHWPE when reinforced with biocompatible material like Zirconia also shows improvement in wear resistance [4] but composite may not act as biocompatible material. PEEK reinforced with the oxidized CF shows reduction in COF by 60 % at 15 % reinforced as compare to unfilled PEEK which is also better than unoxidised state and in case of wear rate, it is found 85 % reduction as compared to unfilled PEEK at 15 % CF reinforcement [5] but it is said that PEEK is not viable as biocompatible material. PTFE also shows reduced in wear up to 162 time and COF (Coefficient of friction) up to 38% when reinforced with 2 wt. % graphite nano particles [16]. UHMWPE and carbon nanotubes composite shows improved mechanical characteristic and wear property but in vitro and vivo test results shows adverse effect [15]. The reinforcement of HAP (Hydroxyapatite) into polymer has shown significant improvement in wear property of matrix material. The reinforcement of HAP into UHMWPE up to 20% has reduction of wear rate up to 60% than pristine form of UHMWPE and also COF of 20 % reinforcement also shows 34 % reduction as compare to its pristine form [2][3].

### Table 1. Implant material Merit and Demerit

| Implant material                     | Merit                                      | Demerit                                    | Reference No. |
|--------------------------------------|--------------------------------------------|--------------------------------------------|---------------|
| Stainless steel                     | Good strength and modulus                  | Corrosive, large wear debris form, aseptic loosening of bone | [6],[7]       |
| Cobalt based alloy                   | Corrosion resistance and sufficient strength. | Releasing harmful ion like Ni, Cr, etc. | [8],[9],[10]  |
| Titanium based alloy                 | Lighter in weight, high strength and resistance to corrosion | Prolong use may cause Alzheimer disease | [9],[11]      |
| HDPE composite and UHMWPE composite  | Lighter in weight, good strength and corrosion resistance | Lack in biocompatible and biodegradable | [2],[12],[13] |
| other polymer composite              |                                            |                                            |               |

The PLA (poly lactic acid) which is thermoplastic and not only biocompatible but also a biodegradable which may be feasible for implant material if it has enough wear resistance. The pristine form of PLA has poor tribolgical properties and it can be improve with the reinforcing material as various other polymer material has proven this phenomenon as mention above, PLA when reinforced with TiO$_2$ grafted flax fibre show enhanced physical and mechanical properties [20]. It is seen that property of PLA can be enhanced with appropriate reinforcement. The PLA/HAP nanocomposite also shows enhanced thermal stability which overcome one of its demerit [14].

In this study, PLA/HAP nanocomposite with different composition as shown in below table no. 2 was studied at parameter of load and frequency as mentioned in section 2.2. The Tribological behaviour of composite was studied for determining percentage feasibility of composite as an implant. The various researchers has found that PLA reinforce with HAP may be suitable for implant or scaffold or tissue engineering application [17] [18] [19].

### Table 2. Material Composition of PLA nanocomposite

| Sample Id | PLA (wt. %) | HAP (wt. %) |
|-----------|-------------|-------------|
| A         | 100         | 0           |
| B         | 95          | 5           |
| C         | 90          | 10          |
2. Experimental details
2.1 Material and Composite preparation
In experimentation, PLA material was chosen as matrix material while Hydroxyapatite (HAP) as a reinforcing material. PLA material was purchased in the form of pallets from additive manufacturing Pvt. Ltd., Hyderabad and HAP was obtain in the form of nanoparticle from Nano research lab, Jharkhand. The properties of HAP nanoparticles are average particle size 20-80 nm with 99.5% purity, molecular formulae as Ca$_5$(OH)(PO$_4$)$_3$, density : 1.038 g/cm$^3$ and melting point: 1100$^0$C. To prepare PLA nanocomposite, HAP with different weight percentage (i.e. 5, 10 and 15) was added into matrix material. To make proper mixing, the mix material was preheated at 50$^0$ to 60$^0$C under stirring mechanism and allowing it to cool at room temperature. Due to this preheating, nanoparticles get adhere to PLA pallets which approximately ensuring proper mixing between both materials.

2.2 Friction and wear test
The preheated composite material was processed through vertical injection moulding machine for preparation of sample. The semi liquid state material was injected into mould cavity and sample with size of 10×10×15 (all dimension are in mm). The semi liquid state was attain approximately at 70$^0$ to 80$^0$ C for pristine PLA while 90$^0$ to 100$^0$ for composite, as reinforcement of HAP increases thermal stability of PLA[14]. The samples of wear was tested on linear reciprocating tribometer (DUCOM) (fig.1) under dry sliding condition and parameter of test was as shown in below table no.3. On basis of pre experimentation, it is found that pristine form of PLA shows significant wear rate in range of load (i.e.70 N to 95 N) and frequency (i.e. 6 Hz to 10 Hz). So, the range of experimentation was selected accordingly to study the effect of reinforcement.

The sample for wear was tested against EN31 plate of 40×40×5 (all dimension are in mm) having high surface finish. Each sample of wear and EN31 was cleaned with acetone before and after test. The specific wear rate was calculated with the (eq.1) as shown below and to measure mass loss, before and after mass was measure by using electronic weighing machine. Each sample was measure for mass three time for improving accuracy. For wear, sample were tested two times and their average reading are taken into count.

\[
Wear\;Rate = \frac{\Delta m \times 10^3}{\rho LF}
\]

where,
Wear rate is in \( \text{mm}^3/\text{Nm} \). Total mass loss (\( \Delta m \)) is in ‘g’.
Density of Composite material (\( \rho \)) in ‘g/cc’. Load (\( F \)) is in Newton.
Sliding distance (\( L \)) = \( 2 \times \text{freq.} \times t \times l \times 10^{-3} \).
Sliding distance is in ‘m’. Frequency (\( \text{freq.} \)) is in ‘Hz’.
Time (t) is in seconds. Stroke length (l) is in ‘mm’.

2.3 Optimization Technique
Design of experiment was planned by using Taguchi technique as it optimises the number of experiment and gives a systematic approach to experimentation. This technique is widely used because it not only reduces the number of test to be performed but also cost and time incurred in doing experimentation. As per the level of design and number of factors that to be examine, it suggest some set of orthogonal array that to be chosen for experiment. In the following experiment, the number of level of design was ‘3’ since there are two composite material and one pristine material while number of factors are three that is reinforcement, load and frequency. Based on above details, L$_9$ was selected as orthogonal array for experimentation in which number of runs are sixteen. After performing all runs, experimental results were analysed by using ANOVA (Analysis of variance) to find influence of each parameters on output. On basis of pre experimentation, it is found that pristine form of PLA shows significant wear rate in range of load (i.e.70N to 95 N) and frequency (i.e. 6 Hz to 10 Hz). So, the range of experimentation was selected accordingly to study the effect of reinforcement.
Figure 1. Linear reciprocating tribometer

Table 3. Experimental Parameters

| Parameters                        | Value     |
|----------------------------------|-----------|
| Reinforcement of HAP nanoparticle (%) | 0, 5, 10 |
| Load(N)                          | 80, 85, 90|
| Frequency(Hz)                    | 7, 8, 9   |
| Stroke(mm)                       | 10 (constant) |
| Time (hr.)                       | 1 (constant) |
| Temperature (°C)                 | 37 (constant) |

3. Result and Discussion

With the help of mass of samples before and after experimentation, the total mass was calculated and by using equation (1), the corresponding wear rate for defined parameter was calculated. The calculated reading was use for optimisation by using Taguchi method. The percentage composition was selected up to 10% because in experimentation it is found that wear rate for 15 wt. % composite increases instead of decreasing. Because of this reverse nature of composite, the 15 wt. % composite was omitted to reduce calculation and error causing in experimentation.

3.1 S/N ratio plot

The Signal to noise ratio is plotted by using Minitab software which minimizes the effect of noise that affecting the results. In this experiment, smaller is better S/N ratio is selected since wear should be small and the equation for smaller is better is mentioned below in equation no. 2. The following table no. 4 shows the corresponding results for all experiments with S/N ratio by using Taguchi technique.

Smaller is better:

\[(S/N)_{LB} = -10 \log \left( \frac{1}{n} \sum_{j=1}^{n} y_j^2 \right) \]  \hspace{1cm} (2)
### Table 4. L_{09} Orthogonal Array with experimental results and S/N ratio

| Reinforcement (%) | Load(N) | Frequency (Hz) | Wear rate \( (mm^3/Nm) \times 10^{-4} \) | SNRA1 | MEAN1  |
|-------------------|---------|----------------|------------------------------------------|-------|--------|
| 0                 | 80      | 7              | 4.0197                                   | -12.0839 | 4.0197 |
| 0                 | 85      | 8              | 4.6595                                   | -13.3686 | 4.6595 |
| 0                 | 90      | 9              | 5.591                                    | -14.9498 | 5.591  |
| 5                 | 80      | 8              | 2.941                                    | -9.3699  | 2.941  |
| 5                 | 85      | 9              | 3.451                                    | -10.7589 | 3.451  |
| 5                 | 90      | 7              | 3.33                                     | -10.4489 | 3.33   |
| 10                | 80      | 9              | 3.891                                    | -11.8012 | 3.891  |
| 10                | 85      | 7              | 3.251                                    | -10.2403 | 3.251  |
| 10                | 90      | 8              | 4.2015                                   | -12.4681 | 4.2015 |

**Graph 1. S/N Plot of experimental results**

The graph (1) shows the main effect plot for S/N ratio for PLA/HAP Nano composite and from the graph the level of factor having highest S/N ration is selected as optimum respond measured. The optimum parameter for wear rate were 5% reinforcement of HAP (level 2), 80 N of load (level 1), and 7 Hz frequency (level 1).

#### 3.2 Analysis of Variance

It is standard statistical technique to interpret the experimental results mainly used to study the relative influences of multiple variables and their significance. It is a statistical tool for testing null hypothesis for designed experimentation, where a number of different variables are being studied simultaneously. This analysis was carried out for a level of significance of 5% i.e. the level of confidence 95%. The results of ANOVA analysis is shown in below table 5, it is suggested that P value less than 0.05 in all parameter will influence the output parameter. Therefore from the results it is clear that reinforcement, load and frequency has influence on wear characteristic of composite material. Below pie diagram
(graph 2) shows the percentage contribution of each parameter on wear rate and it suggest that reinforcement has largest influence on wear property of composite material while both load and frequency comparatively less.

| Source               | DF | Seq. SS | Adj. SS | Adj. MS | F     | P    | % Contribution |
|----------------------|----|---------|---------|---------|-------|------|----------------|
| Reinforcement (%)    | 2  | 13.5919 | 13.8019 | 6.90093 | 231.16| 0.004| 64.34          |
| Load(N)              | 2  | 3.1869  | 3.1869  | 1.59343 | 53.37 | 0.018| 15.085         |
| Frequency (Hz)       | 2  | 4.0772  | 4.0772  | 2.03859 | 68.29 | 0.014| 19.29          |
| Residual Error       | 2  | 0.2697  | 0.0597  | 0.02985 |       |      | 1.277          |
| Total                | 8  | 21.1256 |         |         |       |      | 100            |

**Graph 2. Percentage contribution of factors to wear**

### 3.3 Regression Analysis

The relationship between input and output parameter for PLA/HAP composite was set with the help of linear regression model and equation 3 shows the relation between them. By substituting the values of input variable, we can estimate the predicted value for specific wear rate. The following graph 3 show the graphical comparison between the predicted and experimental specific wear rate.

\[
\text{Wear Rate} = -4.76 - 0.0982 \text{ Reinforcement (％)} + 0.0701 \text{ Load(N)} + 0.401 \text{ Frequency (Hz)} \quad (3)
\]

### 3.4 Confirmation Test

The confirmation was carried out at optimum parameter i.e. for wear rate were 5% reinforcement of HAP (level 2), 80 N of load (level 1), and 7 Hz frequency (level 1). And table 6 shows the comparison between predicted by mathematical model (i.e. eq. 3) and experimentally evaluated specific wear rate.
Table 6. Confirmation test results

| Parameter   | Predicted value | Experimental value | Error % |
|-------------|-----------------|--------------------|---------|
| Wear rate   | 3.164           | 2.935              | 7.21%   |

Graph 3. Experimental vs Predicted wear rate of PLA/HAP nanocomposite

4. Conclusion
The Taguchi technique for optimizing the parameter was significantly analyzed the experimental data and its gives the optimum results for PLA/HAP nano composite for its wear characteristics under dry sliding environment.

- The main effect of S/N ratio plot shows that at optimum percentage of reinforcement is 5%, while load and frequency are optimum at 80 N and 7 Hz.
- It is also seen that beyond 5% of reinforcement the wear behavior of material gets changed that is wear rate increases.
- The experiment also reveals that the PLA/HAP nanocomposite may offer better wear resistance in the range 0 to 5 or 5 to 10 wt. %.
- ANOVA results shows that reinforcement has greater influence while Load and Frequency has less for considered range.
- PLA/HAP nanocomposite exhibits lower wear rate at all its level of experiment as compare to other i.e. pristine form of PLA and PLA with 10 wt. % of HAP nanoparticle.

Acknowledgements
Authors express their gratitude to Government College of Engineering, Aurangabad and Central Institute of Plastic and Engineering, Aurangabad.

References
[1] S. K. Roy Chowdhury, A. Mishra, B. Pradhan, D. Saha, ”Wear Characteristic And Biocompatibility of some Polymer Composite Acetabular Cups”, Wear 256 (2004) 1026-1036.
[2] Liu Jin-Long, Zhu Yuan-Yuan, “Biotribological Behavior of Ultra High Molecular Weight Polyethylene Composites Containing Bovine Bone Hydroxyapatite”, J China Univ Mining & Technol 18 (2008) 0606-0612.
[3] Qinglang Wang, Jinlong Liu, Shirong Ge, “Study of Biotribological Behavior of the Combined Joint Of Coctina And Uhmwpe/Bha Composite in a Hip Joint Simulator”, Journal of Bionic Engineering 6 (2009) 378-386.
[4] Kevin Plumlee, Christain J. Schwartz, “Improved Waer Resistance of Orthopedic Uhmwpe By Reinforcement Of Airconium Particles”, Wear (2009) 710-717.
[5] Xiaoduao Zhao, Dansheng Xiong, Xinxin Wu, “Effects of Surface Oxidation Treatment Of Carbon Fibers On Biointertribological Properties of C/PeeK Materials”, Jornal Of Bionic Engineering 14 (2017) 640-647.

[6] P. Christel, A. Meunier, A.J.C. Lee (Eds.), “Biological and Biomechanical Performance of Biomaterials,” Elsevier, Amsterdam, The Netherlands, 1997, pp. 81–86.

[7] Kalpana S. Katti, “Biomaterials in total joint replacement”, Colloids and Surface B: Biointerfaces 39 (2004) 133-142.

[8] Ramsden, J. J, Allen D. M, Stephenson D. J, Alcock J. R, Fuller, G. N., Goch, G. D. “The Design and Manufacture of Biomedical Surfaces,” CIRP Annals-Manufacturing Technology, 2007. 56(2):687-711.

[9] Sachin G. Ghalme, Ankush Mankar, and Yogesh Bhalerao, “ Biomaterials in Hip Joint replacement,” International Jornal of Materials Science and Engineering, volume 6, June 2016.

[10] Ozturk, O., Turkan, U., and Eroglu, A. E., “Metal ion release from nitrogen ion implanted CoCrMo orthopaedic implant material,” Surface & Coatings Technology, 2006. 200(20-21):5687-5697.

[11] Eisenbarth, E., Velten, D., Muller, M., Thull, R., Breme, J. “Biocompatibility of a stabilizing elements of titanium alloys,” Biomaterials, 2004. 25(26):5705-5713.

[12] Roy S, Pal S., “Characterization of silane coated hollow sphere alumina-reinforced ultra high molecular weight polyethylenecomposite as a possible bone substitute material”. Bull Mater Sci, 2002, 25(7): 609–612.

[13] Hashimoto M, Takadama H, Mizuno M, et al., “Titanium dioxide/ultra high molecular weight polyethylene composite for bone-repairing applications: preparation and biocompatibility.” Key Engineering Materials, 2003(240/242): 415–418.

[14] Ming Gong, Qian Zhao, Liming Dai, Yingying, Tingshun Jiang, “Fabrication of Polylactic acid/ Hydroxyapatite/graphene oxide/ composite and its thermal stability, hydrophobic and mechanical properties.” Journal of asian Ceramic Societies 5, (2017) 160-168.

[15] Kanagaraj, S., Mathew, M. T., Fonseca, A., Oliveira, M. S., Simoes, J. A., Rocha, L. A.. “Tribological characterisation of carbon nanotubes/ultra high molecular weight polyethylene composites: the effect of sliding distance.” Int J Surf Sci Eng. 2010, 4(4- 6):305-21.

[16] R.K.Goyal, M.Yadav, “ The wear and friction behavior of Novel Polytetfluroethylene/ expanded Graphite Nanocomposite for tribological application,” Joournal of tribology, April 2014, Vol. 136/021601-1.

[17] Siriporn Tanodekaew, Somruethai Channasanon, Pakkanun Kaewkong, Paveena Uppanan, “PLA-HA scaffolds: preparation and bioactivity”, Procedia Engineering 59 (2013 ) 144 – 149.

[18] Maria Persson, Gabriela S. Lorite, Hana E. Kokkonen, Sung Woo Cho, “ Effect of bioactive extruded PLA/HA composite film on focal adhesion formation of preosteoblastic cells,” Colloids and Surface B: Biointerfaces 121 (2014) 409-416.

[19] Ming Gong, Qian Zhao, Liming Dai, Yingying Li, Tingshun Jiang, “Fabrication of polylactic acid/hydroxyapatite/graphene oxide composite and their thermal stability, hydrophobic and mechanical properties,” Journal of Asian Ceramic Societies 5 (2017) 160–168.

[20] MReza Foruzanmehr, Pascal Y. Vuillaume, Säid Elkoun, Mathieu Robert, “Physical and mechanical properties of PLA composites reinforced by TiO2 grafted flax fibers”, Materials and Design 106 (2016) 293–304.