

Tribological Evaluation of Nano Crystalline Hydroxyapatite Composite for Break Lining Application

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Abstract

Composite materials are potentially attractive for a wide range of medical and mechanical applications. In the present investigation Hydroxyapatite (HA) composite have been successfully prepared by a sol-gel auto combustion and sol-gel method respectively. This prepared material was characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Transmission Electron Microscopy (TEM). Friction and wear characteristics of HA composite were determined using a pin-on-disc tribometer at applied loads of 50-110 N. Result show that the wear performance of HA was superior and obtaining lower friction coefficients than the WM. To calculate the wear depth by Archard wear model FEA is done. It has observed that no significant difference in between experimental and numerical wear depth.

Keywords: *Solution Combustion, Sol-gel, Hydroxyapatite, Composite, Pin-on-disc, Tribology, FEA, Biomedical applications.*

INTRODUCTION

Bio-ceramic is an important subset of biomaterial which is used for replacing and damaged part of the musculo skeletal system. The importance of Bio-ceramics

in biomedical applications have been universally accepted as it shows an excellent biological, mechanical and biochemical properties [1]. Bio-ceramics can be divided into two large groups: Bio-

inert and bioactive ceramics [2]. Bio-inert ceramics have no influence on the surrounding living tissues. In opposite, the bioactive ceramics are able to bond with living tissues. Hydroxyapatite (HA) and Willemite (WM) are two bioactive ceramics.

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ has excellent biocompatibility and surface active properties with living tissues, it has become one of the most important bio-ceramic materials for artificial bone [3]. The chemical composition of bone is similar to HA [4]. HA is the main constituent of bone cement, but the basic brittleness and poor strength of HA restrict its bio-medical applications under load and friction conditions [5]. Joints grafting such as a knee, hip is an effective surgical treatment to relieve pain and to restore the locomotion function for patients with unused joints. An ideal bone implant should be osteoinductive, resorbable and easy to shape, and possessing adequate mechanical properties [6].

Artificial HA is widely used in a field of bone tissue engineering [7, 8]. The HA is also used as ion-exchanger, catalyst and adsorbent [9-11]. In addition, recent studies prove that HA particles are used for anti-cancer treatment [12]. Willemite

(WM), Zn_2SiO_4 , also known as zinc orthosilicate, is the main constituent of crystalline glazes seen in modern day pottery [13]. WM is also known as Glass ceramics. Glass ceramics such as WM having good mechanical strength, high colour purity, high luminescence efficiency strong chemical durability, and highly thermal stabilities and these properties are suitable for different applications [14-15]. WM exists in three different phases which are α , β and γ - Zn_2SiO_4 and shows three different colours of emission: α - Zn_2SiO_4 (green Emission), yellow emission (β - Zn_2SiO_4), and red colour (γ - Zn_2SiO_4).

In the earth's crust Silicate minerals are found abundantly. Research on WM ceramics have been considered to be technologically and biologically important; because of the extraordinary properties of materials possess electrical conductivity, good mechanical strength, thermal conductivity, dielectric properties and a low coefficient of thermal expansion [16]. They are ionic crystals; possess tetrahedral SiO_4 or complex molecules formed by the coupling of SiO_4 tetrahedral. From one to five valence cations can be bonded to produce a very large variety of silicate crystals [17]. Pure WM is a silicate of individual unlinked

silicon tetrahedral. Each zinc is also at the centre of the oxygen tetrahedral of almost the same size as the silicon tetrahedron.

Every oxygen has one silicon and two zinc atoms at the corners of a triangle. Potential fields of application for WM are pharmaceuticals or biological, optoelectronics, optics and medical diagnostics [18-20].

Tribology is a branch of science and technology of interacting surfaces in relative motion and of related subjects and practices. There are three parameters of tribology friction, wear and lubrication [21]. The tribological behaviour of HA investigates by many works. Qian Zhao et al [22] studied the effect of CNT addition on coefficient of friction of HAcomposites against a stainless-steel ball. Zhi Lu et al [23] analysed micro-tribological properties of HA-based composites in ball-on-block tribometer and describe the relationship between the load and the wear resistant. J. Zheng et al [24] micro-tribological properties of artificial HA and human tooth enamel and found an enamel having significant plastic deformation than HA at low load.

HA has been synthesized by many routes, including co-precipitation [25], sol-gel

synthesis [26], emulsion methods [27], microwave precipitation [28] and mechanochemical methods [29]. A large number of research efforts have been focused toward the preparation of important materials, mostly oxides with improved properties by using the solution combustion method [30]. In solution combustion synthesis, aqueous reactive solutions are used, where the precursors are mixed on the molecular level. The advantage of this process has been demonstrated by the use of different fuels and oxidizers, varying the oxidizer/fuel ratio and ignition sources, as well as a combination of various synthesis approaches [31].

Willemite has been synthesized by many routes, such as hydrothermal method [32], ball mill [33], solid-state reaction method [34] and sol-gel synthesis [35]. Sol-gel synthesis method has lowest processing temperature method and performed with solvents such as alcohol, ionic liquid and water. The significance of sol-gel method is that it is performed in a solvent at ambient pressure, while in solvothermal and hydrothermal methods tend to use high pressures and high temperatures. Sol-gel literature shows that crystallization of Zn_2SiO_4 requires at least temperatures of around 1000°C. Sol-gel methods have the

advantage of providing characteristic particles such as spherical particles, uniform shapes, or Nano-sized particles by varying the some experimental conditions; they may be combined with the other synthesis routes in the future [36].

In the present study, HA and WM were prepared by sol-gel auto combustion and a sol-gel method respectively. This work focuses on study of the tribological parameter of HA and WM under different loading condition on pin-on-disc tribometer.

To prepare a pin of HA and WM acrylic material used .The (90:10) composition were used to prepare a pin. To find pressure distribution on pin FEA is done. Archard wear model is used to find the wear depth numerically.

EXPERIMENTAL

Chemical

For synthesis of composite Tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$; TEOS, Sigma-Aldrich and purity $\geq 99\%$), Zinc chloride (ZnCl_2 , Thomas baker AR grade), HCL and distilled water used and Calcium nitrate tetra hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Thomas baker AR grade), di-Ammonium hydrogen orthophosphate ($(\text{NH}_4)_2\text{HPO}_4$, Thomas baker AR

grade) and polyvinyl alcohol (PVA, Thomas baker AR grade) used for Hydroxyapatite. All chemicals used here were of analytical grade and used without further purification.

Synthesis of Hydroxyapatite

Hydroxyapatite (HA) was prepared by modifying solution combustion method. For this, polyvinyl alcohol (PVA) was used as a fuel. In brief, the stoichiometric amounts of the nitrate precursors $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and phosphate precursor $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in double distilled water to form the solution of 0.1 M. The equimolar solution of PVA was prepared in double distilled water. The mixture of oxidants and fuel was placed onto a magnetic stirrer for 30 min to get uniform mixing.

Evaporation of water to form a gel of precursors was carried out at 100°C and then the gel was heated at 300°C to obtain a powder. The obtained powder of HA was then annealed at 950°C for 6 h to remove carbon residues and then used for further analysis. The dried mixture possesses the characteristics of combustion and can be ignited to start the combustion reaction using muffle furnace. This method is reported previously by researcher[37].

Synthesis of Composite

Willemite (WM) was synthesized by sol-gel method. For this Tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$) was first partially hydrolysed at a molar ratio of TEOS: water: =2.40:0.25 and HCL are used as a binder in the solution. 2 mol zinc chloride dissolves in pre-hydrolyzed solution. This mixed solution stirred for by a magnetic stirrer to form a homogeneous solution. After stirring the mixed solution is refluxed at 350c for until gel formation. Formed gel dried in the oven at 3000c. The resulting powder was then annealed in the temperature range of 500°–1200 °C for 2 h with a heating rate of 5°C min. This method is reported previously by researcher [38].

Characterizations

The structural and morphological studies of the samples were studied using X-ray Diffractometer (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Phase identification and structure analysis of Hydroxyapatite and Willemite were studied using X-ray diffraction (Philip-3710) with Cu-K α radiation in the 2 θ range from 10 to 60. The pattern was analysed by X-pert Highscore plus software and compared with the Joint Committee on Powder Diffraction Standards (JCPDS)

(JCDPScardno.01-074-0565 and 01-075-0278).

The surface morphology and particle sizes of the Hydroxyapatite and Willemite were determined by using transmission electron microscope (Philips CM 200 model) with an operating voltage of 20–200 kV and a resolution of 2.4 Å. The compositional analysis was done by energy dispersive spectroscopy (EDS, JEOLJSM6360).

Wear Test

Investigation of tribological parameters were carried out using a pin-on-disc Tribometer [39]. The image of the tribometer used is shown in Fig. 1. HA and Composite were used as the friction material and gray cast iron material used for the disc. The disc had a size of 165 mm in diameter, 8 mm in thickness and the hardness of 62 HB. The normal load is applied to pin through loading lever which is a single bar with specimen holder fixed at one end and at the other end it carries a wire rope for suspending dead weight's to apply normal load. Rotational speed and time of revolution are applied through controller, which is connected to a machine. The disc was connected to a motor through a variable speed clutch capable of imparting speeds up to 2000 rpm to the disc. The LVDT (Linear

variable differential transducer) and load cell measure wear and frictional force which is displayed on the controller. Graphical representation of wear and frictional coefficient are visible on a PC. The frictional surface of the disc was abraded with a 320 grade abrasive paper and was cleaned by a dry cloth before each test in order to start with same surface roughness.

Pin Preparation

The nanoparticles of HA and Composite are used for pin preparation. In this powder of ceramic material and acrylic material (90:10) were used for pin preparation, when they are mixed together they were formed a semisolid mass. This semisolid mass is pressed in a die by UTM at 0.3 ton load. Formed pins have 10 mm diameter and 20 cm in length.



Fig. 1 Apparatus of pin on disc tribometer.

The X-ray diffraction (XRD) pattern of the pure HA is given in fig. 2 (a).XRD spectra were recorded in the 2 theta range 10-60 and step size of 0.02. The main phase, in the samples was identified as Hydroxyapatite (JCDPS No.01-074-0565). The crystallite size of HA was calculated

from full width half maximum of the strongest diffraction peak using Debye-Scherrer formula [40]. The crystallite size of HA is 34.50 nm. About pure HA similar result and phase purity were observed in reported work [41-42]

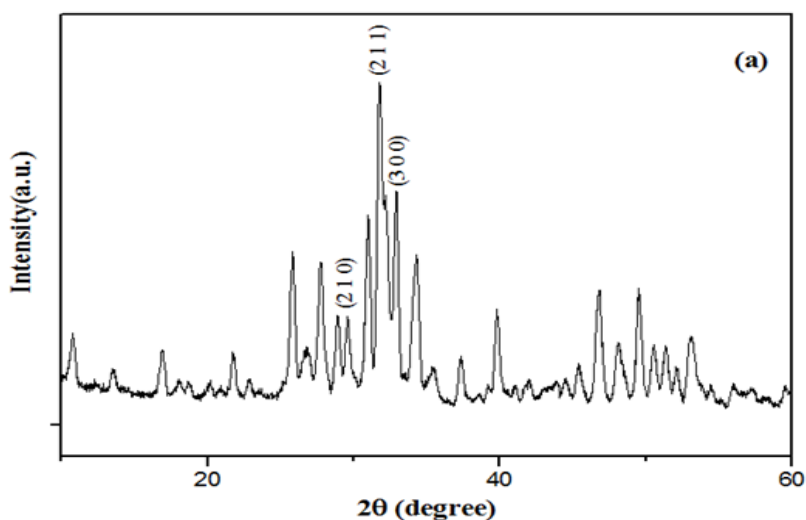


Fig. 2(a) XRD pattern of HA

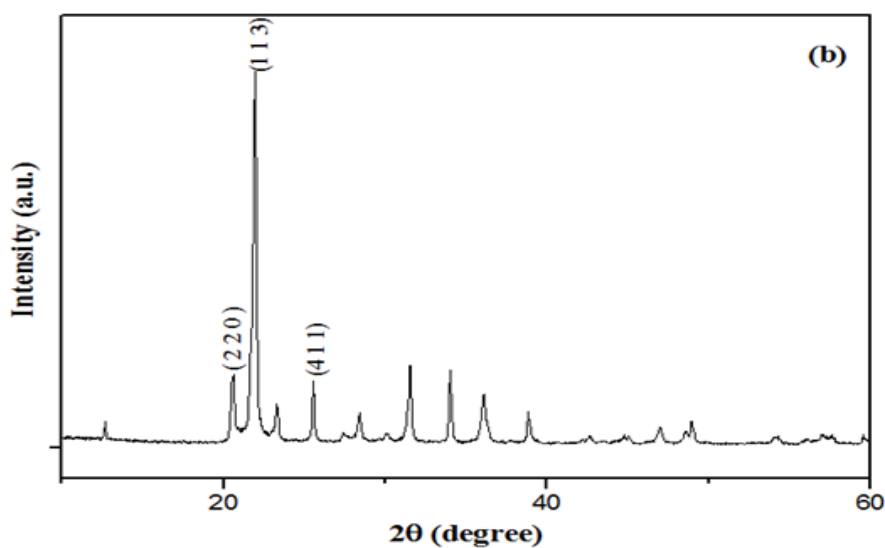


Fig. 2(b) XRD pattern of Composite

The XRD pattern of the pure composite sample is shown in Fig. 2 (b).The main

phase, in the sample was identified as Willemite (JCDPS no. 00-037-1485).

There are no secondary phases observed in the sample.

Willemite showing a rhombohedral structure with space group R-3. It can be seen that, the lattice parameters of the prepared sample is in excellent agreement with standard data $a=13.93 \text{ \AA}$, $c=9.3100 \text{ \AA}$.

The crystallite size of Willemite was calculated from full width half maximum (FWHM) of the strongest diffraction peak using Debye-Scherrer formula [40]. The crystallite size of Composite is 38.42 nm . About Willemite similar result was observed in reported work [43].

SEM analysis

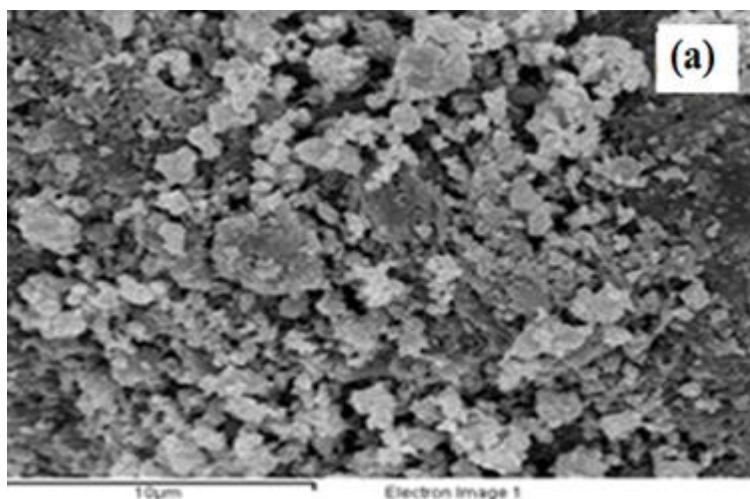


Fig. 3(a) Scanning electron microscopy (SEM) images of HA

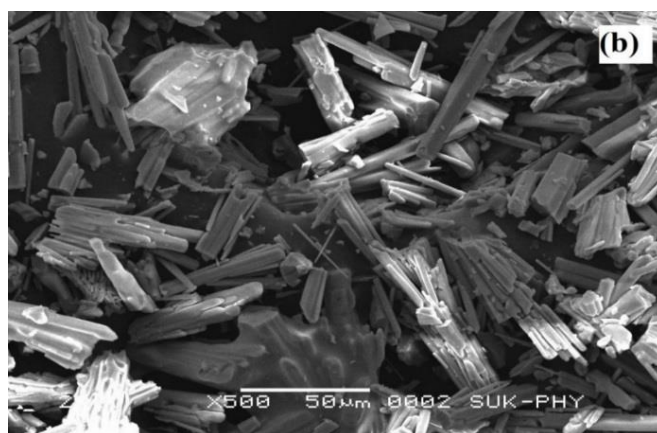


Fig. 3(b) scanning electron microscopy (SEM) images of Composite

The Scanning electron Microscopy (SEM) technique was used to observe and analyse the microstructure, agglomeration and particle size of HA and composite. In fig. 3 (a) and (b) SEM micrographs of hydroxyapatite samples are shown similar agglomerates that are consisting of fine crystallites. SEM micrographs of composite show Rod like crystalline structure with an average length of less than 50µm.

Composition analysis of pure HA and composite is carried out by EDS technique. The EDS pattern for pure HA and composite is shown in fig. 4 (a) and (b) and the detail composition is given in Table. 1 from the data it is confirmed that HA is composed of Ca, P, O & composite composed of Zn, Si and O. The Ca/P atomic ratios for HA is 1.69 which is near about the standard 1.67[1]

Table.1 Atomic percentage composition

Name	Ca	P	O
Hydroxyapatite	38.68	22.89	38.43
Name	Zn	Si	O
Willemite	14.23	20.58	58.15

EDS Analysis

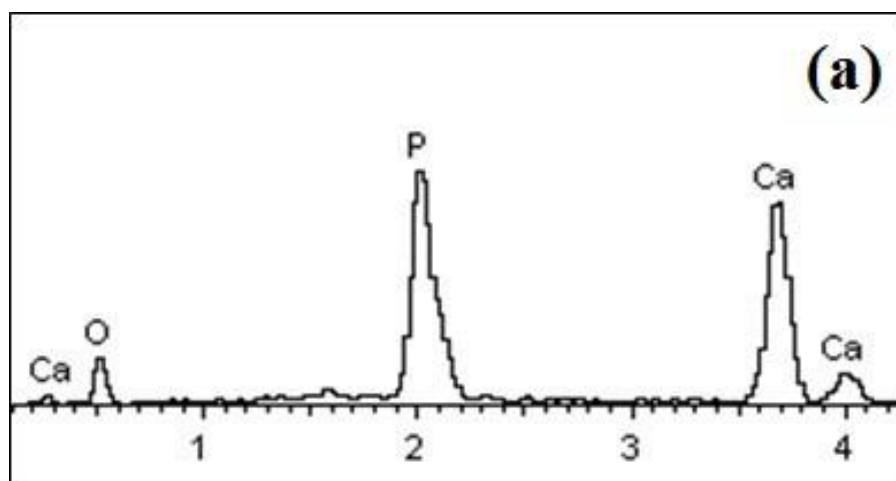


Fig. 4(a) EDS analysis of HA

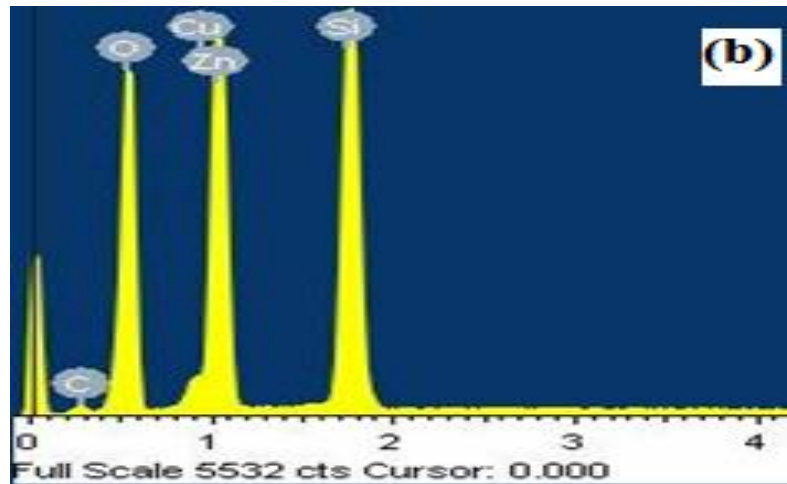


Fig. 4(b) EDS analysis of Composite

TEM studies.

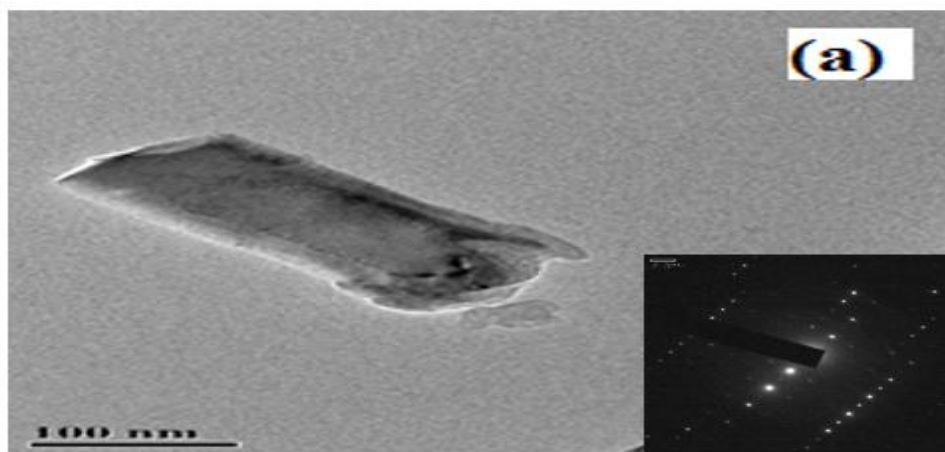


Fig.5 (a) TEM images of HA

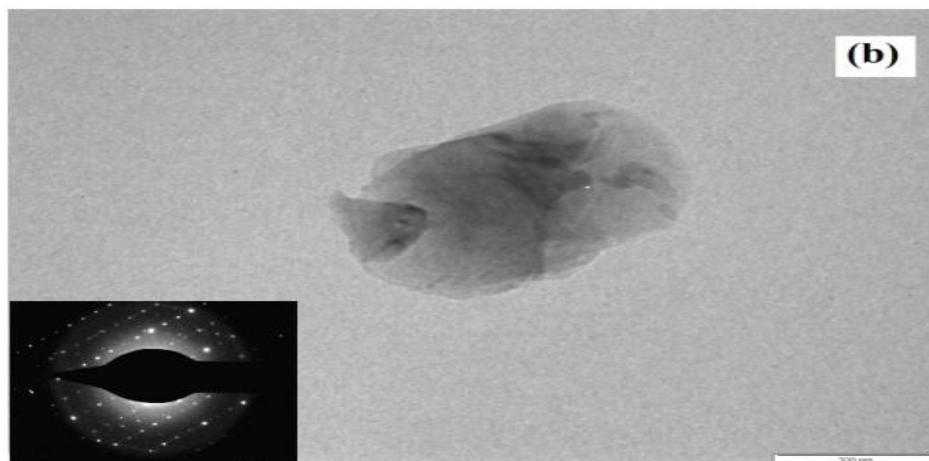


Fig.5 (b) TEM images of Composite (Inset: corresponding SAED pattern.).

The particle size of HA and Composite were estimated from TEM analysis. Fig.5 (a) and (b) shows TEM micrographs of HA and composite. The HA and composite nanoparticles were a cylindrical rod-like shape with homogeneous microstructure. HA particles have size less than 100nm in diameter. However, the particles composite were found around 200 nm in diameter.

The diameters of the particles are slightly larger than the observed crystal sizes obtained from XRD, due to the high-temperature calcination which causes the grain growth. The corresponding SAED pattern (inset of Fig. 5 (a) and (b)) shows bright ring patterns indicating the polycrystalline nature of nanoparticles, which is in good agreement with XRD results.

TRIBOLOGY TEST

The variation of friction coefficients of HA and composite with sliding distance under different loads is shown in Fig. 6 (a) and (b), respectively. It can be seen that the HA shows lower coefficients at the low load and it increases with the increasing load. It is seen that there is gradually increasing the friction coefficient of HA as sliding distance increase. On the other hand, WM composite exhibits different behaviour, with its friction coefficient increasing gradually first and then decreasing over the sliding distance. The friction coefficients for composite were constant for 70 and 110 N at 100 and 250m and at 366m constant for 70 and 90N. Friction coefficients of composite at 50 and 110 N have less fluctuation. From both the graphs, it is clear that the friction coefficient of both material increase as load increase over a sliding distance.

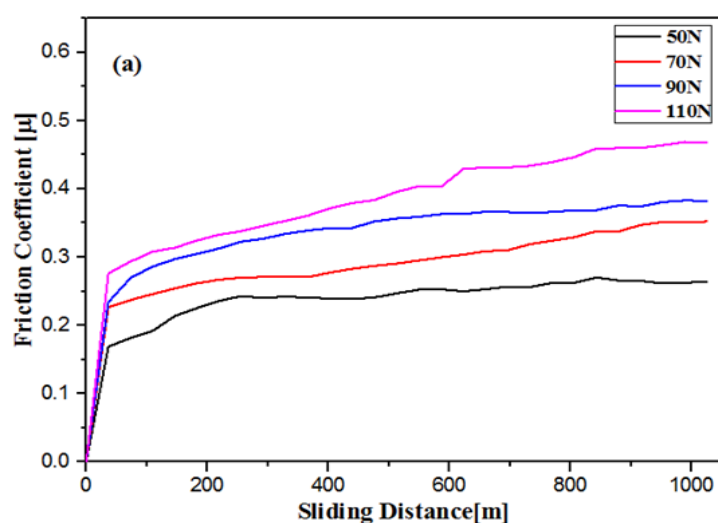


Fig. 6 (a) Friction coefficients of HA

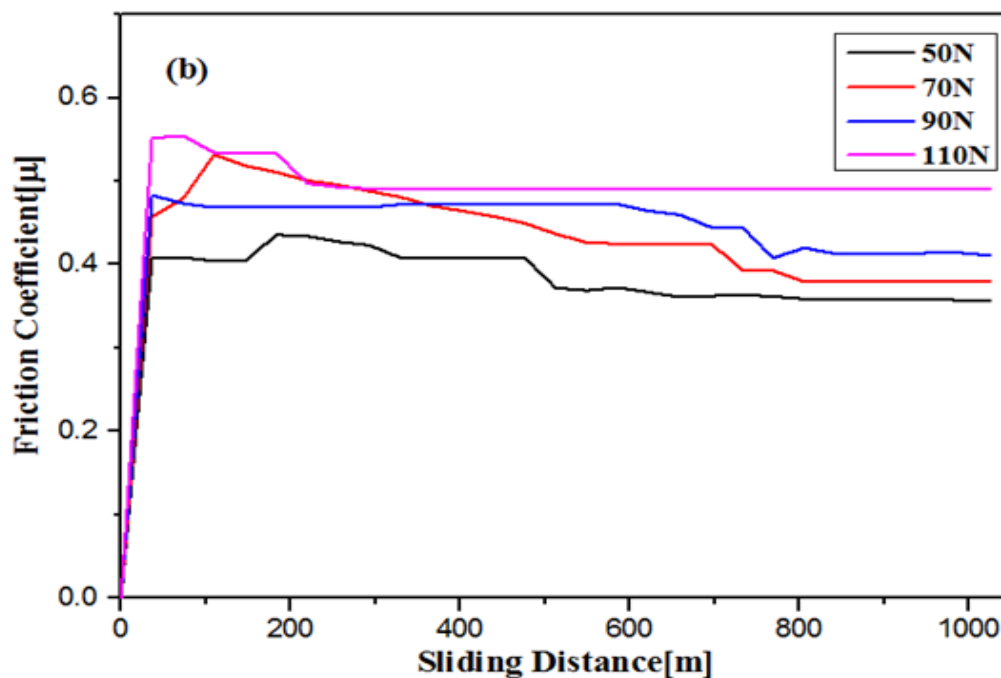


Fig. 6 (b) Friction coefficients of composite

Table 2 presents a summary of the average value friction coefficients and Wear rate. Wear rates for HA and composite are shown in Fig. 7. It is clear that wear rate of composite is higher than HA, which is in agreement with their high friction coefficient of friction values. The wear rate of both the material is increased as applied load increase.

Also, Theoretical calculations are used to calculate wear rate of specimens. Table. 3 shows Total mass loss grams of the specimen are taken by performing experimentation on Tribometer and wear depth.

The volume loss of specimen can be calculated as

$$\text{Volume loss} = \frac{\text{Mass loss}}{\text{Density of Pin}}$$

Now, Depth of wear rate of specimen is calculated by

$$\text{Volume of pin} = \pi * r^2 * h$$

r= Radius of pin

h= height of pin

Hence, it's possible to calculate the depth of wear experimentally.

Table. 2 Comparison of Friction Coefficient and Wear rate of HA and composite

Load	HA		WM composite	
	Friction Coefficient (μ)	Wear rate, 10^{-5} ($\text{mm}^3(\text{Nm})^{-1}$)	Friction Coefficient (μ)	Wear rate, 10^{-5} ($\text{mm}^3(\text{Nm})^{-1}$)
50	0.2340	0.98	0.3734	3.25
70	0.2856	1.4	0.4247	3.87
90	0.3312	1.63	0.4369	4.22
110	0.3786	1.78	0.4832	4.45

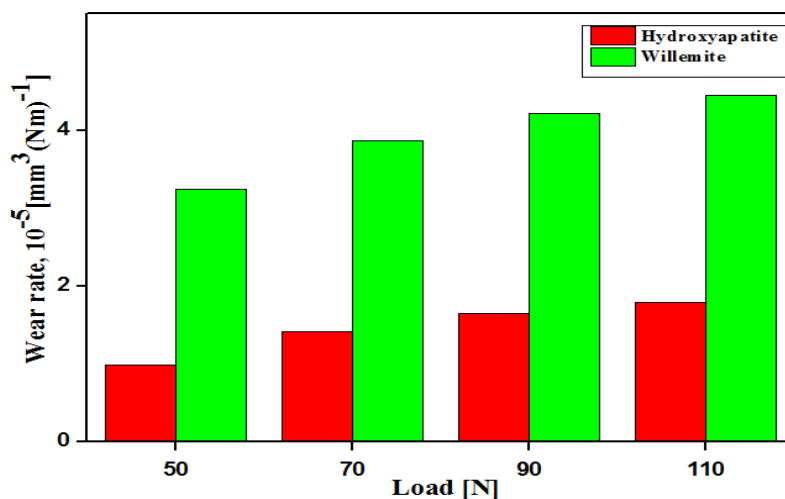


Fig. 7 Wear rates of HA and composite

Table. 3 Experimental wear depth

Samples	Load (N)	Total mass loss grams	Depth of Wear in mm
HA	50	0.001	6.25
	70	0.002	12.51
	90	0.003	18.17
	110	0.004	25.03
WM	50	0.003	18.85
	70	0.005	31.42
	90	0.007	43.99
	110	0.009	56.56

NUMERICAL ANALYSIS USING FEA

A static analysis using Ansys calculates the effects of steady loading conditions on a structure. The static analysis determines the displacements, pressure, stresses, strains, and forces in structures or components caused by loads that do not

induce significant inertia and damping effects.

The flow chart of the steps used for static analysis, consisting of a series steps was shown in Fig. 9 and table. 4 consist material property used for analysis.

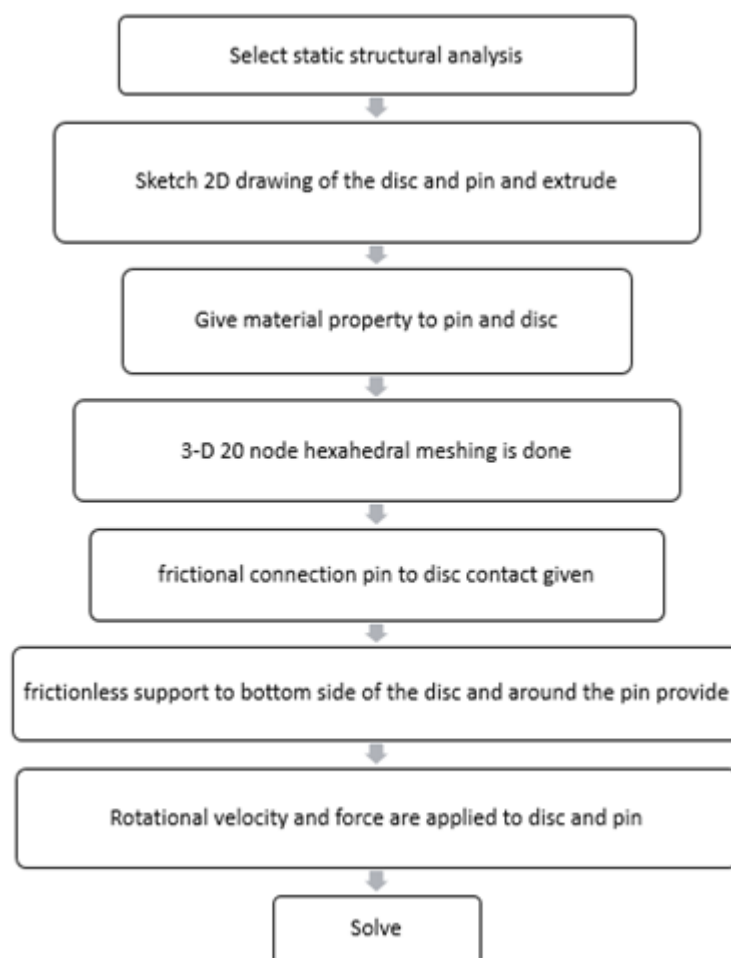


Fig. 8 Flow chart of the static structural analysis

Table 4 Material property used for an alysis

Parameter	HA	composite	Gray cast iron
Young's modulus	40 GPa	37.5 GPa	110 GPa
Poisson's ratio	0.28	0.3	0.3
Density	2.034 g/cm ³	2.026 g/cm ³	6.850g/cm ³

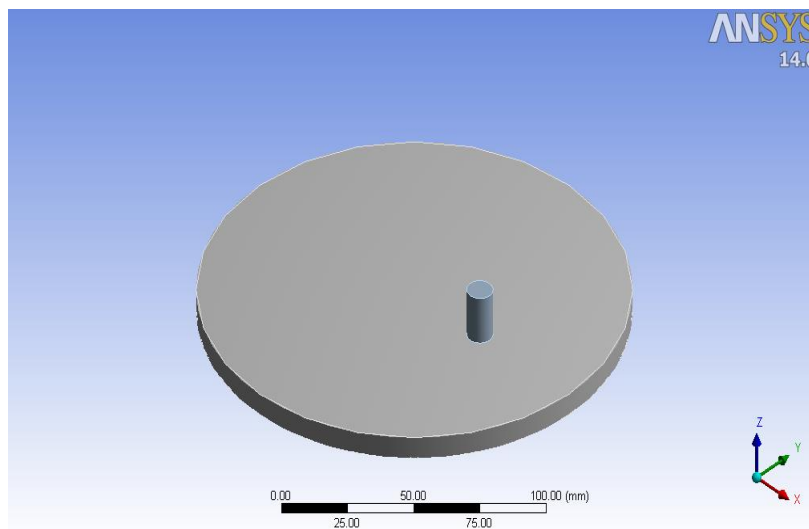


Fig. 9 3D solid model of Tribometer

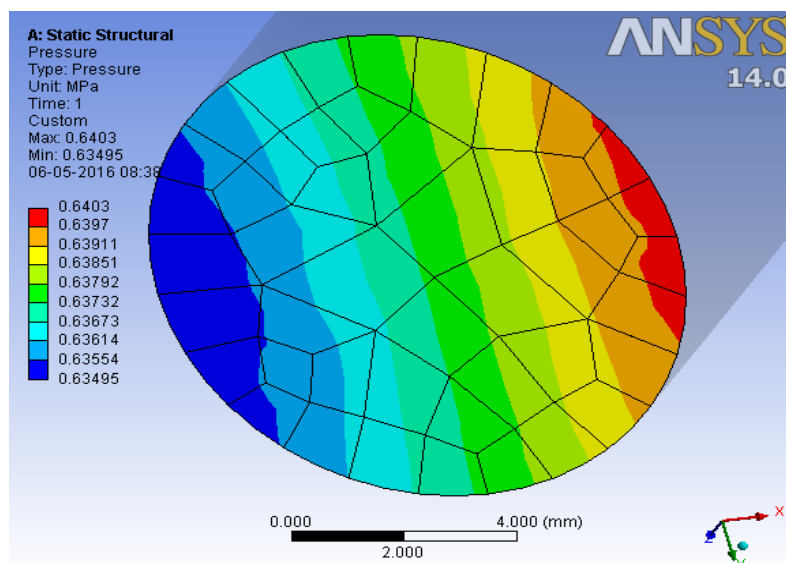


Fig. 10 Contact pressure distribution in an interfacing of pin and disc

Fig. 9 shows the solid model of Tribometer in an x-y plane. From this, we observe that a pin is perfectly flat contact with the rotating disc at 70 mm track diameter and Fig. 10 shows the contact pressure distribution on an interfacing surface of pin in contact with the disc

Form above solution, we got maximum pressure value. So, putting this Value in Archard equation [44], we get the depth of wear.

The depth of wear rate calculated as follows

$$\text{Depth of wear } h = K * P * S$$

Where,

K = wear coefficient in m²/N

P = contact pressure distribution in N/m²

S = sliding distance in meter (1000m)

Wear coefficient:

1. Wear coefficient

$$= \frac{V'}{S * F_n}$$

Where,

V' = measured wear volume

S = sliding distance

F_N = applied load

Now, putting all these values in an equation we got,

The final CAD model is prepared from the dimensions are taken from Tribometer test setup. First disc has created with 165 mm diameter with 8 mm thick and pin of 10 mm diameter and 20 mm thick.

Table 5 Numerical Wear Depth

Sample	Load N	Maximum Contact pressure in MPa	Wear coefficient m ² /N	Depth of Wear in mm
HA	50	0.6403	9.8328*10 ⁻¹⁵	6.29
	70	1.0324	1.40469*10 ⁻¹⁴	14.5
	90	1.3273	1.63880*10 ⁻¹⁴	21.75
	110	1.5823	1.78778*10 ⁻¹⁴	28.28
WM	50	0.6701	2.96150*10 ⁻¹⁴	19.84
	70	0.9648	3.52555*10 ⁻¹⁴	34.01
	90	1.2096	3.83898*10 ⁻¹⁴	46.43
	110	1.4843	4.03840*10 ⁻¹⁴	59.88

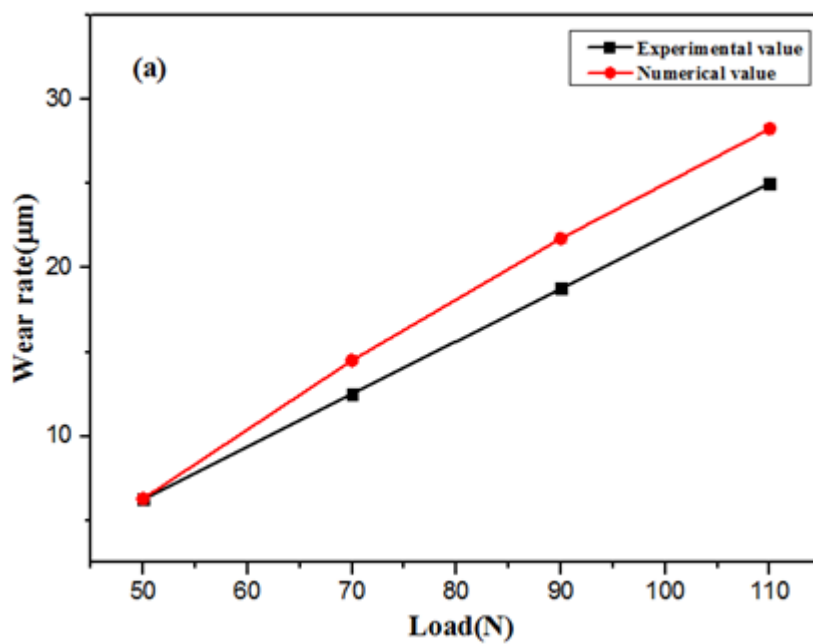


Fig. 11(a) Comparison of Experimental and Numerical results HA

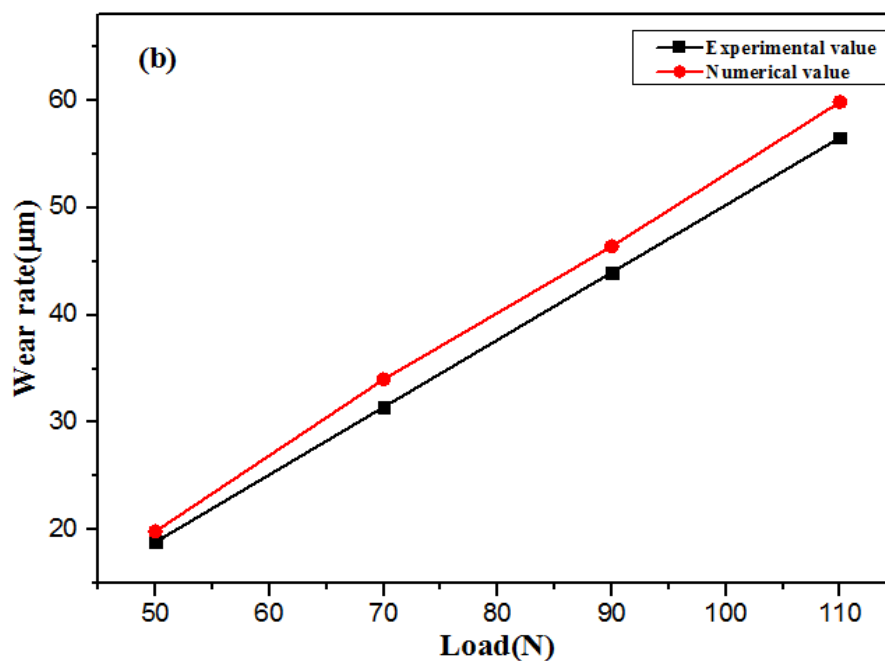


Fig. 11(b) Comparison of Experimental and Numerical results composite

From the fig. 12, it has observed that no significant difference in between Numerical and Experimental result. In numerical result have errors occurred in

terms of modelling, meshing strategy and depends upon operator skill, but have many advantages compared with experimentation. Numerical result is useful

to give a result at various times that are difficult, expensive or time consuming to study using experimental techniques. Numerical predictions for wear rate are useful for all desired quantities, high resolution in time, portable, easy to modify and cheap in cost. Also, it is fast and used for multiple purpose compare with experimental results. The numerical analysis does not replace measurement completely, but amount of experimentation and cost significantly reduce.

CONCLUSIONS

In the present research work HA and WM were successfully prepared by the conventional sol-gel auto combustion and a sol-gel method respectively. We are able to prepare pin of both materials using acrylic repair material. EDS studies confirmed the presence of HA and composite. The friction and wear properties of HA and WM were studied in dry medium. Friction test showed that the friction coefficient of HA is smaller than composite. The friction coefficient of both material goes on increasing as load increases. The wear rate of HA is much lower than the composite. As the load increases wear rate of HA and composite goes on increasing. It is observed that there is no significant difference in between wear depth calculated by

experimentally and numerically. Hence, it is revealed that HA is potentially applicable as a friction material in engineering application also, in biomedical application than composite.

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