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Evaluation of Tribological Behaviour of Nano-Crystalline Hydroxyapatite and Graphene Doped 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 and Graphene doped Hydroxyapatite have 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 50N, 70N, 90N and 110N. Result show that the wear performance of graphene doped HA was superior and obtaining lower friction coefficients than the HA. It has observed that no significant difference in between experimental and numerical wear depth.

Keywords- Hydroxyapatite, Composite, Pin-on-disc, Tribology.

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I. INTRODUCTION

Bio-ceramic is an important subset of biomaterial which is used for replacing and damaged part of the musculoskeletal system. The importance of Bio-ceramics in biomedical applications has 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 shows no influence on the surrounding living tissues. In opposite the bioactive ceramics are able to bond with living tissues. Hydroxyapatite (HA) and Graphene doped HA are two bioactive ceramics. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ 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]. 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 [7]. The tribological behaviour of HA investigates by many works. Qian Zhao [8] studied the effect of CNT addition on coefficient of friction of HA composites against a stainless-steel ball. Zhi Lu[9] analyzed micro-tribological properties of HA-based composites in ball-on-block tribometer and describe the relationship between the load and the wear resistant.

In the present study, HA and Graphene-doped HA were prepared by sol-gel auto combustion and a sol-gel method respectively. Proposed work is to be study the tribological parameter of HA and graphene doped HA under different loading condition on pin-on-disc tribometer. To prepare a pin of HA and Graphene-doped HA acrylic material used. The (90:10) compositions were used to prepare a pin. Archard wear model is used to find the wear depth numerically.

1.1. Motivation of research

Initially in a braking system asbestos fiber was used as a friction material which was banned in 1986, by Environmental protection agency as the asbestos fiber can lodge in the lung and produce adverse respiratory condition. Later semi-metallic and Kevlar are used as friction material. These material having high wear rate, limited temperature range and produce noise during braking.

1.2. Problem identification

Ceramic lining is costly and generally used in sports car. The aim of the work is to produce alternate ceramic friction lining material which will be costly, lower wear rate, higher temperature range and producing no noise.

The objective of this study is being address to the following

1. Synthesis or formation of film of nanostructured and porous Graphene mixed composite by non-conventional methods such as sol-gel auto-combustion method.

2. Characterization of graphene mixed composite by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Electron Dispersed spectra (EDS).

3. Study of the friction and wear properties of pure composite and grapheme mixed composite by pin on disc tribometer for mechanical applications.

2. MATERIALS AND METHODS

2.1. Materials

For synthesis of composite Tetraethyl orthosilicate Si $(OC_2H_5)_4$; TEOS, Sigma-Aldrich and purity ≥99%), Zinc chloride ($ZnCl_2$, Thomas baker AR grade), HCL and distilled water used and Calcium nitrate tetra hydrate Ca $(NO_3)_2.4H_2O$, Thomas baker AR grade), di-Ammonium hydrogen orthophosphate ($(NH_4)_2HPO_4$, 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.

2.2. Pin Preparation

The nanoparticles of HA and Composite are used for pin preparation. Here powder of ceramic material and acrylic repair material (90:10) were used for pin preparation, when they are mixed together they were formed a semisolid mass. This semisolid mass press in a die by universal esting machine (UTM) at 3000kg load. Formed pins have 10mm diameter and 20mm in length.

2.3. 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 $Ca(NO_3)_2.4H_2O$ and phosphate precursor $(NH_4)_2HPO_4$ were dissolved in double distilled water to form the solution of 0.1M(molar). 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 is carried out at 100°C and then the gel was heated at 300°C to obtain a powder. The obtained powder of HA then annealed at 950°C for 6h 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 [13].

2.4. 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 Graphene-doped HA were studied using X-ray diffraction (Philip-3710) with Cu-Kα (λ=1.54178 Å) radiation in the 2Theta range from 10^0 to 60^0. The pattern is analysed by X-pert High score plus software and compared with the Joint Committee on Powder Diffraction Standards (JCPDS) (JCDPS#01-074-0565 and JCDPS#01-075-0278). The surface morphology and particle sizes of the Hydroxyapatite and Graphene-doped HA were determined by using transmission electron microscope (Philips CM 200 model) with an operating voltage of 20 to 200kV and a resolution of 2.4Å. The compositional analysis is done by energy dispersive spectroscopy (EDS, JEOLJSM6360).

2.5. Wear Test

Investigations of tribological parameters were carried out using a pin-on-disc tribometer [19]. The image of the tribometer used is shown in fig. 1.

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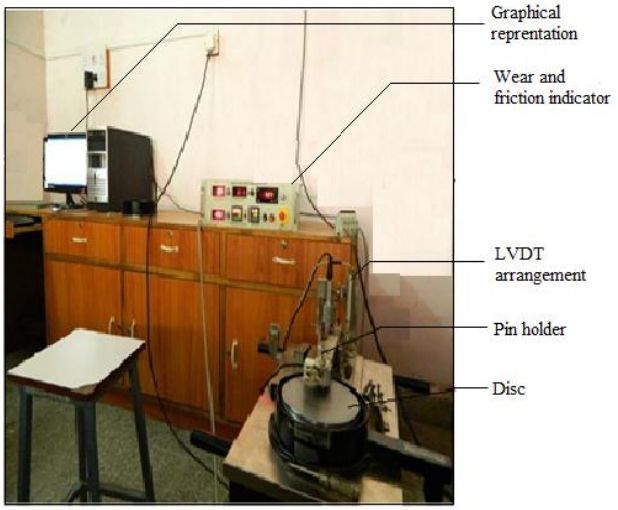

Fig. 1. Pin on disc Tribometer setup

The disc had a size of 165 mm in diameter, 8mm in thickness and the hardness of 62 BHN. 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 weights 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 display screen. The frictional surface of the disc is 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.

3. RESULT AND DISCUSSION

3.1. Physical and chemical properties

3.1.1. XRD analysis

The X-ray diffraction (XRD) pattern of the pure HA is given in fig. 2. XRD spectra were recorded in the 2theta range 10^0 to 60^0 with step size of 0.02. The crystallite size of HA was calculated from full width half maximum of the strongest diffraction peak using Debye-Scherer formula [14].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad [1]$$

where D is the crystallite size, λ is the wavelength of Cu-Kα radiations (λ=1.5405 Å), theta is the corresponding Braggs diffraction angle and β is full width at half maxima of the most intense peak (211).The crystallite size of HA is 34.50 nm. About pure HA similar result and phase purity were observed in reported work [15][16].

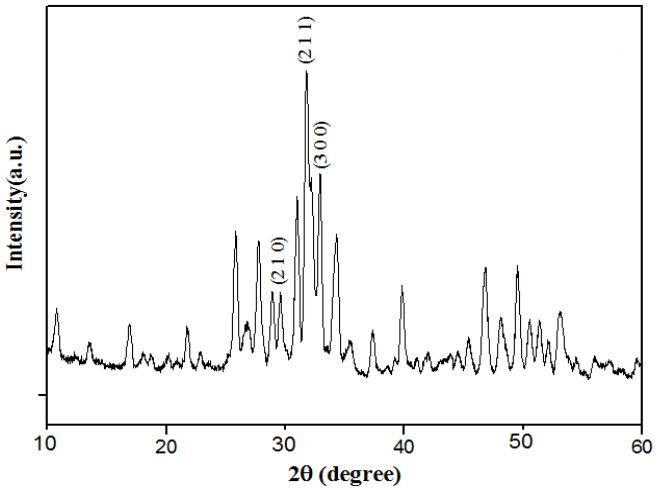

Fig. 2. XRD pattern of (a) HA

The main phase, in the samples was identified as Hydroxyapatite (JCDPS#01-074-0565). The XRD pattern of the pure composite samples is shown in fig. 3. The main phase, in the sample was identified as Graphene-doped HA (JCDPS#00-037-1485). There are no secondary phases observed in the sample.

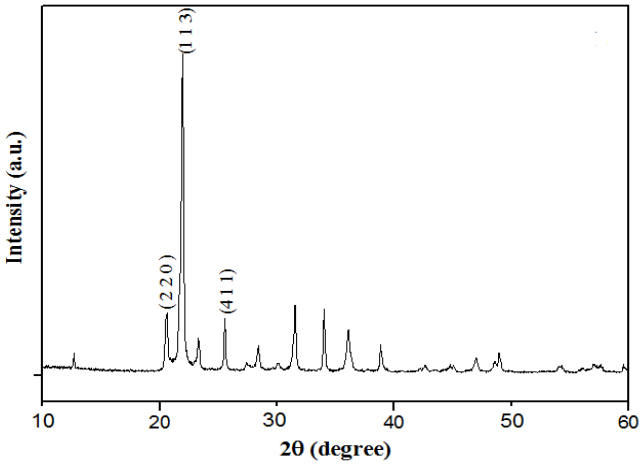

Fig. 3. XRD pattern of 1% graphene doped HA

Graphene-doped HA showing a rhombohedral structure with space group R-3. It can be seen that, the lattice parameters of the prepared sample are in excellent agreement with standard data a=13.93Å, c=9.3100Å. The crystallite size of Graphene-doped HA was calculated from full width half maximum (FWHM) of the strongest diffraction peak using Debye-Scherer formula [14]. The crystallite size of Composite is 38.42 nm. About Graphene-doped HA similar result was observed in reported work [18].

3.1.2. EDS analysis

The EDS analysis was performed for specimens and typical results have been selected and presented in table 1. The evaluation of elemental constituents of pure HA revealed peaks belonging to calcium, phosphorus and oxygen. From EDS spectra pure HA had a Ca/P ratio of approximately 1.69. These findings suggest that value for HA crystals are closer to expected value for molar ratio of calcium to phosphorus in stoichiometric HA (Ca/P =1.67)[1].

Table 1 Atomic composition

composition	Elements		
	Ca	P	O
Hydroxyapatite	38.68	22.89	38.43

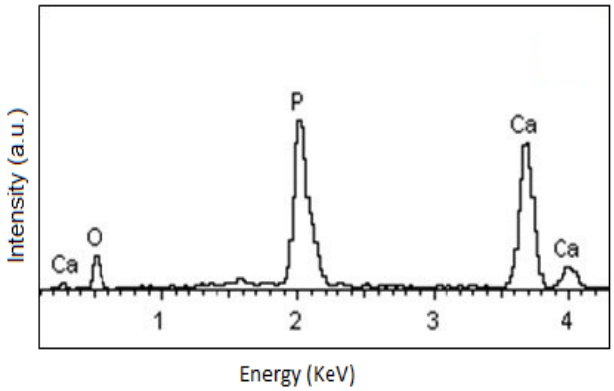

Fig. 6. EDS spectra of pure HA

3.2. Microstructural properties

3.2.1. SEM analysis

The Scanning Electron Microscopy (SEM) technique was used to observe and analyses the microstructure and particle size of HA and composite.

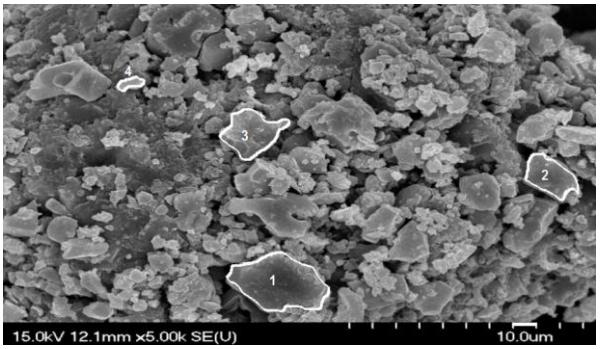

Fig. 4. Scanning electron microscopy (SEM) images of HA

In fig. 4. SEM micrographs of hydroxyapatite samples are shown similar agglomerates that are consisting of fine crystallites. It shows size of grain selected as 1,2,3,4 is approximately 30µm, 20µm, 20µm and 10µm respectively. In fig.5, SEM micrographs of composite show Rod like crystalline structure with an average length of less than 50µm.

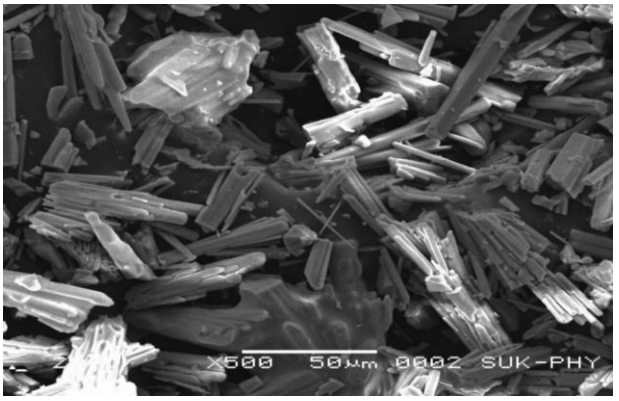

Fig. 5. Scanning electron microscopy (SEM) images 1 % graphene doped HA

3.2.2. TEM analysis

The particle size of HA and Composite were estimated from TEM (Transmission electron microscopy) analysis. 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 200nm in diameter.

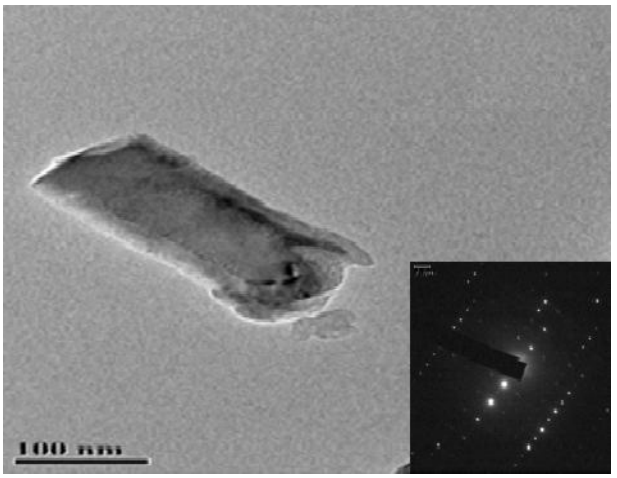

Fig. 7. TEM images of HA

(Inset: corresponding SAED pattern)

Fig. 7. and fig. 8. shows TEM micrographs of HA and composite respectively.

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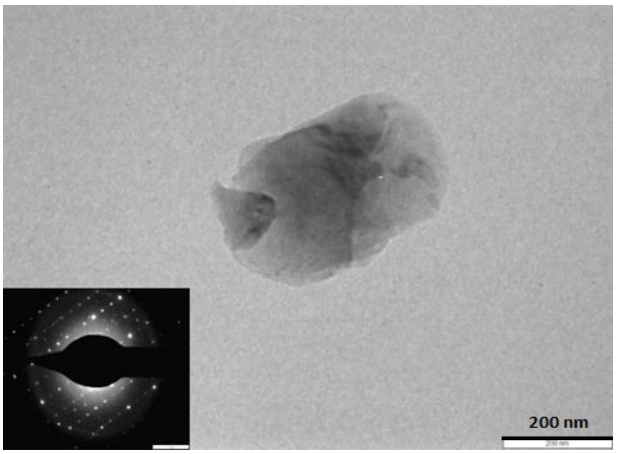

Fig. 8. TEM images of 1 % graphene doped HA

(Inset: corresponding SAED pattern)

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. 7. and fig. 8.) shows bright ring patterns indicating the polycrystalline nature of nanoparticles, which is in good agreement with XRD results.

3.3. Mechanical properties

3.3.1. Tribology test

The variation of friction coefficients of HA and composite with sliding distance under different loads is shown in fig. 9 and fig.10, 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 Graphene-doped HA exhibits different behavior with its friction coefficient, increasing gradually first and then decreasing over the sliding distance.

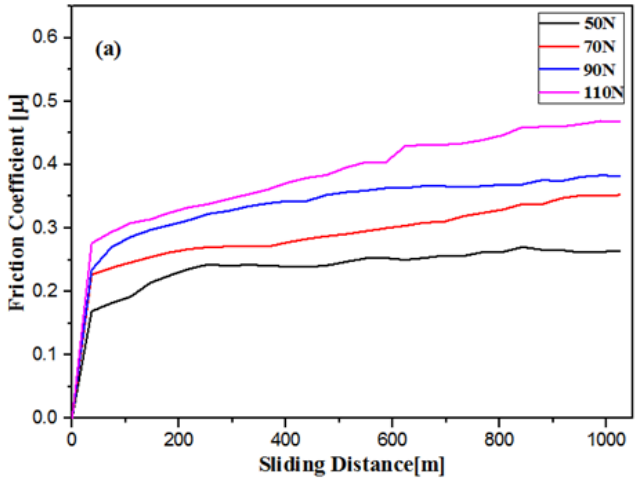

Fig. 9. Friction coefficients of HA

Table 2 Comparison of Friction Coefficient and Wear rate of HA and 1 % graphene Doped HA

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

The friction coefficients for graphene doped HA are constant for 70N and 110N at 100m and 250m. These are constant for 70 and 90 N. 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 materials increase as load increase over a sliding distance.

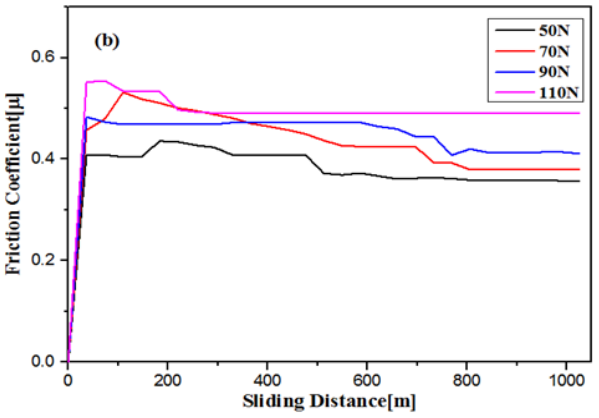

Fig. 10. Friction coefficients of 1 % graphene doped HA

Table 2 represents a summary of the average value friction coefficients and wear rate. From wear rates for HA and composite, it is clear that wear rate of composite is higher than HA, which is in agreement with their high 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(in grams) of the specimen are taken by performing experimentation on tribometer and wear depth.

Table 3 Experimental wear depth variation with load.

Load	HA		Graphene-doped HA	
	Friction Coefficient (μ)	Wear rate $\times 10^{-5}$ (mm^3/N-m)	Friction Coefficient (μ)	Wear rate $\times 10^{-5}$ (mm^3/N-m)
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

The variation in wear rate with time shows life of brake pad.In fig. 11. wear rate of pure HA is shown. It shows that wear rate continuously increases with load and distance travel. The plots of wear rate as a function of sliding distance (0 to 3000m) composites for load of 50N, 70N, 90N and 110N have been shown in fig. 12. The sliding wear data of pure HA and Graphene doped composites are considered for interpretation.

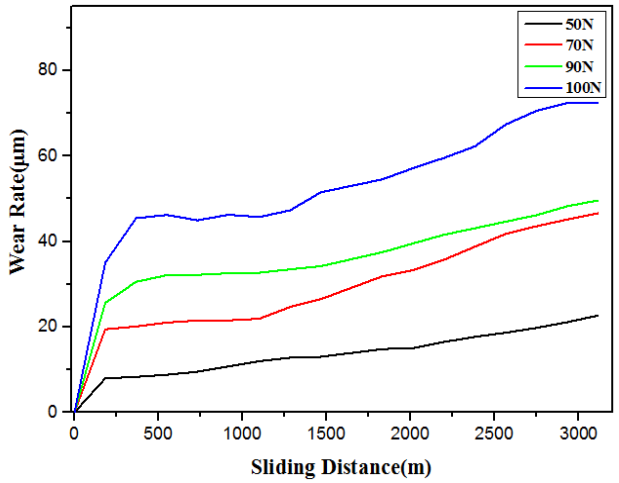

Fig. 11. Wear rate of pure HA Vs Distance

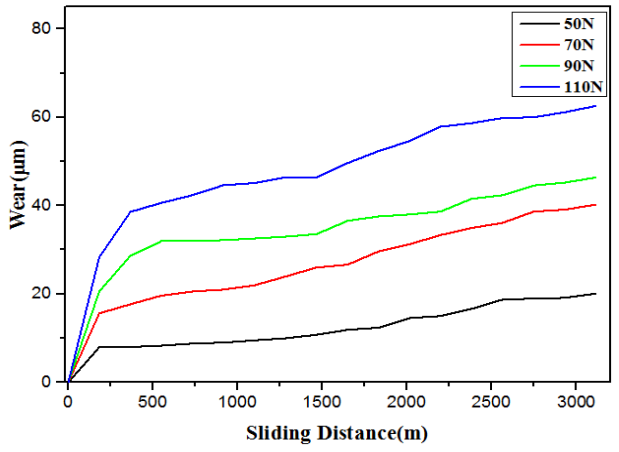

Fig. 12. Wear rate of 1% graphene doped HA Vs Distance

The graph of wear verses distance of 1% graphene doped are displayed in fig. 12. In this graph wear rates of different trend for same loading conditions and operating conditions have taken. The wear rates of graphene doped HA are less compared to Pure HA.

It is evident that the friction coefficient increases after the incorporation 1% of graphene content in the composites. This behavior is obviously relevant to the self-lubricating ceramics and wear resistant property of graphene which can reduce the adhesion between the composite with the metallic counterpart.

The variation in coefficient of friction as a function of Load is shown in fig.13 & fig.14. As the real area of contact and shear strength of composite substrate changes during sliding, the coefficient of friction increases with increase in sliding load. Similar trends were observed at other sliding distances and velocities investigated during the current studies.

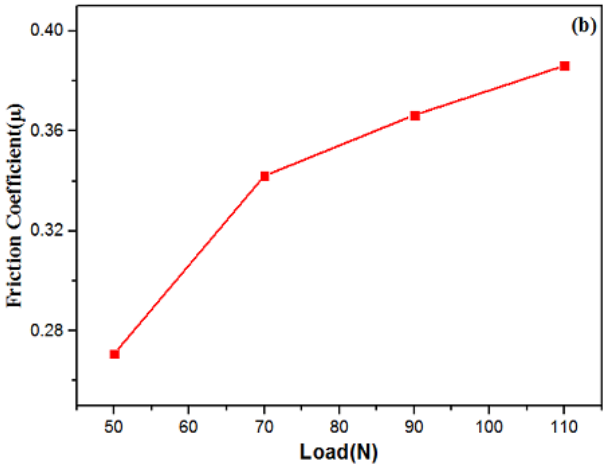

Fig. 13. Friction Coefficient of Vs Load

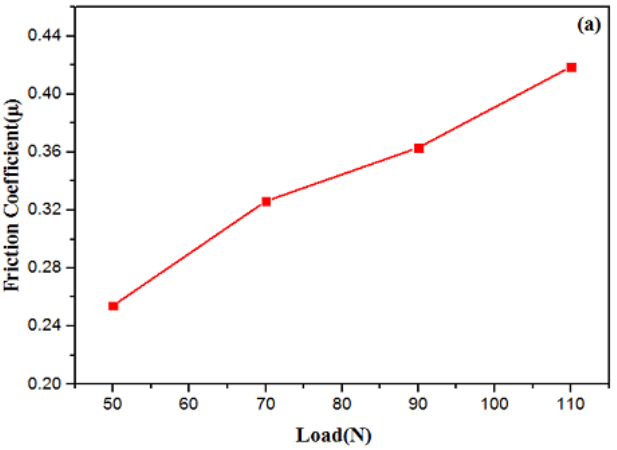

Fig. 14. Friction Coefficient of 1% Graphene-HA Vs Load

The maximum wear resistance and minimum friction values were achieved with 1 % Graphene doped composites; this was because the lower particle size (30μm–40 μm) filler was uniformly distributed on the surface of the composites, this also acted as a self-lubricating agent

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4. SUMMERY AND CONCLUSION

4.1. Summary

For the synthesis of Non-asbestos friction lining materials different methods are used. In present investigation with the help of sol-gel auto combustion method pure HA and graphene doped composite material was successfully prepared. Composite material has synthesized using various ingredients are grapheme, resin, ceramic, aramid fiber and calcium precursors. The required test carried out on a tribometer. After completing experimental results are interpret, discussions have presented and conclusion is to be find out.

4.2. Conclusion

The conclusions obtained from experimental, XRD, SEM and TEM wear surface analyses conducted in this research are as follow

1) From XRD graph it shows Pure and Graphene Doped Composite material having pure phases, no impurities were present in the Nano powder.

2) SEM monographs shows porous nature it shows agglomeration nature.

3) From TEM images it shows size near about 200nm.

4) Friction test showed that the friction coefficient of 1% Graphene HA is smaller than HA.

5) The wear rate goes on increases with load.

6) The friction coefficient of both material goes on increases as load increases.

7) The high COF and less wear rate observed at a composition of 1 % of graphene doped Composite, because of excellent friction stability and anti-fade properties of Ceramic composite.

8) Coefficient of friction decrease with decreasing Grapheme% because of its less stability at high temperature and less bonding characteristics.

9) The stability of friction film formation of two disparate fibers is based on the electrostatic attraction of Graphene and Ceramic whiskers.

The effective method of wear simulation is very significant to quickly interpret measured data in practical application.

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