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Enhancement of Mechanical and Tribological Properties of SU-8 Polymer using Graphene Filler

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Abstract— in this work, surface micromechanical properties of different polymeric coatings (SU-8 resin and their composites with Graphene, Boron nitride etc.) on glass substrate will be examined using nanoindentation and pin-on-disc tribometer. The thicknesses of such coatings were 30-35 µm which will be done using spin coater. The load–unload responses will be used to extract their elastic modulus and hardness values using nanoindenter. Induced micro-structural differences in coatings will be confirmed using scanning electron microscopy (SEM). These measurements will be used to explain the differences in the tribological performance between different coatings. Such correlation is useful for more complex and application-specific tribological experiments. Both elastic modulus and hardness of SU-8 are increased after adding graphene filler and coefficient of friction is reduced at lower load and higher speed SU-8/graphene (5wt %) composite

Index Terms— SU-8, Polymer, MEMS, Graphene, Tribology, Elastic Modulus and Hardness

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1 Introduction

SU-8 is a material which lies in polymeric group of material. Its properties such as mechanical strength, thermal stability, easy fabrication etc are best in all polymer material such as PMMA (polymethylmethacrylate), PTFE (Polytrifluroether) etc. Previously MEMS industry was used silicon as a structure material but it has several disadvantages such as difficult in structural fabrication etc i.e. in this present era SU-8 is used for next generation structural material for MEMS. It has various advantages over Si, used as micro electro material system (MEMS) such as bio-compatibility, close to hydrophobic nature etc and also have the potential in fabrication of structural material for MEMS such as micro gears, accelerometer etc [1-6]. It's a negative epoxy based photoresist. The initially SU-8 is developed by IBM in 1982. It consist of eight epoxy in bisphenol- novalac glycidyl ether (Each molecule consist of 8 epoxy group i.e. the names is SU-8) which is shown in Figure 1. For making highly cross linked, it is pre-baked, exposing under the ultra violet (UV) rays followed by post baking [10].

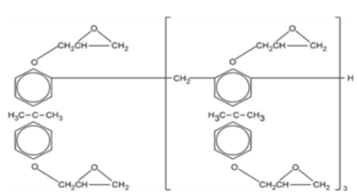

Figure 1: Sturcuture of SU-8

It has only two disadvantage which are (1) Poor Tribological properties such friction and wear (2) Poor Mechanical Properties such elastic modulus (E) and hardness (H). Therefore, a researcher thinks to remove these two drawbacks of SU-8 by adding solid lubricant and liquid lubricant. Solid lubricants are graphite, graphene and multi wall carbon nano tube and liquid lubricants are PFPE (perfluropolyethylene), base oil etc. There are very literature are available in the field of improvement of mechanical as well as tribological properties. First we discussed about the improvement of tribological properties of SU-8. A very few researchers who were added nano particles and liquid fillers in a different weight percentage and made a SU-8 composite such as;

S jiguet et al [7-8] added wt% 2.5 & 5 silica nano particles on SU-8 and conducted the experiment on sliding friction apparatus using carbon steel & polyoxymethylene (POM) balls of 6mm diameter. From these experiments, They observed the following points such as heat treatment of surface reduces wear rate, for low wear the optimal concentration of silica nano particles is consider, the coefficient of friction of composites depends on the ball counter face and elastic modulus of SU-8 and also reported that there is no correlation between mechanical behaviour and wear of material. In further study they developed SU-8 structure on aluminium, quartz & silicon wafers by photolithography method and performed experiment on same setup using Inox & polyoxymethylene (POM) balls of same diameter. In this study they reported that nanoparticles reduce coefficient of friction by a factor of ~ 5 in comparison to unreinforced SU-8 and wear rate also.

Further R. Arvind Singh et al. [9] tried to improve tribological property using surface chemical treatment (using ethanolamine-sodium phosphate buffer) which change the surface property. The chemically treated surface sample was further dip coated in PFPE solution by dip coating method for lubrication purpose. They performed the tribology test on Ball-on-Disk machine using Si3N4 Balls of 4 mm diameter. After conducting all test on surface, they reported that steady state coefficient of friction was reduced by ~ 4 to 5 times and increased the surface hydrophobicity and wear life.

After self assembled monolayer of PFPE on the surface which reduced the coefficient of friction drastically and increased wear life further P. Saravana et al. [14-17] added PFPE inside SU-8 and made SU-8 nano composite (CNT, graphite, SiO2). This type of lubrication is known as in-situ lubrication. They conducted tribology test on Ball-on-Disk tribo-machine using Si3N4 Balls of 4 mm diameter and characterized the tested sample by using 3D optical profilometer, scanning electron microscopy, nanoindentation etc. They reported that decrease in initial coefficient of friction, increase in surface energy after wear and wear life. In further study they used different lubricant oil [PFPE, Base Oil & MAC (multiply alkylated cyclopentane)] inside the SU-8 and made composite in which the tribology test was performed on the same setup sated above. In this work, they reported that drastically reduction in initial and steady-state coefficient of friction and wear life increased by ~ 5 times for wt%10 of lubricant PFPE. They also studied in-situ heating effect on SU-8/PFPE composite using tribometer and reported that initial and steady state Coefficient of friction was reduces by ~2 & ~7 times respectively and also wear life was increased by 3 times.

The second important property of SU-8 which is very poor is mechanical property (elastic modulus and hardness). There are very few researchers who added nano particles and liquid filler in a different weight percentage and made SU-8 composite such as S jiguet et al [7-8] added wt% 2.5 & 5 silica nano particles on SU-8 and reported that coefficient of friction depends upon elastic property of SU-8 material. Further they studied the structure of SU-8 which is made by photolithography on aluminium, quartz and silicon surface. They conducted the stress test on the surface of SU-8 composite and reported that these particles reduce the internal stress and coefficient of thermal expansion from 50 ppm/0C to 27 ppm/0C. As we know the in this present era various nano particles are available such as carbon fillers (graphite, graphene and single wall and multi wall carbon nanotube (SWCNT and MWCNT) etc), diamond like carbon (DLC) etc. Therefore, further study was done by H. C. Chaimori et al. [11] who studied coating of SU-8 and nano particles (Diamondoids, SWCNT & gold nanosphere) means SU-8 composite and made the ASTM tensile standard sample. The tensile test was performed by micro universal tensile test machine. They were reported that effective modulus of SU-8 decreases with addition of nanoparticles at low weight percentage and decrease the elastic modulus of SU-8/SWCNT composite.

A. T. Al-Halhouli et al. [12] analyzed the hardness of SU-8 by Oliver-Pharr method using Nanomechanical tribometer in which Berko-vich indentor tip was used. They reported that elastic modulus, hardness, energy storage modulus & energy loss modulus were reduced very marginal amount. Further M. Mionic et al. [13] studied mechanical response of SU-8/CNT composite using nano indentation test using Nanomechanical tribometer in which Berko-vich indentor tip was used. The MWCNT on SU-8 is mixed with the help of different solvent. These solvents are gamma butyrolactone, propylene glycol methyl ether acetate, methyl-ethyl ketone and acetone. They were evaporated with the help of baking over 24 hr. They reported significant increase in elastic modulus where acetone & PGMEA solvent are use which shows young modulus is significant depend upon solvent vapour pressure.

Above we discussed the solid lubricant such as silicon particles, carbon nanotube either single wall or multi wall, diamond like carbon but now we will discussed liquid lubricant such as PFPE, base oil SN-150 etc. The very few researchers used liquid fillers such as P. Saravana et al. [14-17] added PFPE as liquid filler for improvement of mechanical properties and made SU-8/PFPE composite with or without solid lubricant. The mechanical test conducted on nanoindenter using Berkovich indentor which consist diamond tip. They reported that mechanical properties (elastic modulus and hardness) were marginally increased. Further they also performed the in-situ test on SU-8 lubricant composite using different liquid such as base oil; PFPE and MAC (multiply alkylated cyclopentane) and performed the test on same nano indentation machine using Berkovich indentor and obtained marginally increased in hardness of SU-8/PFPE composite from pure SU-8. Further study by adding carbon fillers was carried out by Jitendra K Katiyar et al. [18-21]. They reported that 10 wt % of graphite composite gives lower coefficient of friction and good wear resistance. However, no comprehensive work has been reported for the improvement in mechanical properties of SU-8 especially using graphene materials as the filler.

The main objective of this present research, the surface micromechanical properties of coating play a crucial role in the reliability of products to which they are applied. Thin film coating is progressively being applied in today's advanced products. However, they have not been widely used for tribological applications. They have great potential in providing low friction and low wear properties to materials for applications in micromechanical devices, food process, extreme environments etc. where tradition lubricants are not desirable or applicable.

2 Experimental Methadology

2.1 Material Selection

Glass substrate of ~ 3 x 3 cm (normal glass slides) was use to deposited 30-35 µm thick SU-8 or SU-8 composite films. The thickness was large enough to avoid any substrate effect on the properties of materials. The carbon nano powder such as graphene is used in fabrication of SU-8 composite. The particle size of graphene (Reinste nano ventures pvt Ltd, Noida India) powder is <100nm.

2.2 Surface Preperation

Glass specimens were sliced into ~3 cm x 3 cm pieces. The entire glass specimen were thoroughly cleaned with deionized water by use of Ultrasonicator for 15-20 min followed by acetone cleaning and finally dried at room temperature. The oxygen plasma treatment was done after cleaning of glass for about 5-7 minutes using plasma cleaner PDC 32G (Harrick plasma, NY, USA). There are two main objective of oxygen plasma treatment (1) to remove the foreign particles and (2) to generate -OH groups on the surface which improve the adhesion in between substrate and coating. The plasma treated glass wafers were then subjected to spin coating immediately on S-2000 series (MILLMAN, Pune India) spin coater of SU-8 and its composite (Grade 2025, Microchem Ltd USA). The parameters for spin coating was stage-1 speed 300 rpm for duration of 15 seconds, followed by stage-2 speed 1000 rpm for the duration of 70 seconds which produced coating film of thickness ~35-40 microns respectively of SU-8 and its composite. The spin coated SU-8 and its composite samples were prebaked at temperature of 70 0C for 5 minutes followed by at 95 0C for 10 minutes. The prebaked SU-8 and its composite samples were exposed to UV (ultra violet) rays which properties are wavelength 365 nm and power 210 mJ/cm2 for duration of 40-60 seconds using UV lamp. A UV exposed SU-8 and its composite samples were carried out for post exposure bake at a temperature of 70 0C for 5 minutes followed by 110 0C for 15 minutes. All post exposure bake samples were stored in the desiccators before any further analysis. All the procedure and parameters of spin coating, prebaking, UV curing and post backing was approximately same for both pure SU-8 films and its composite films.

In this present work, for making of the SU-8 composites, wt% 5 of graphene was added to SU-8 (Grade 2025, Microchem Ltd USA) after measuring from mirco-balance (Citizen, India) and then powder was thoroughly mixed using stirring process in SU-8 for 25-30 minutes before spin coating. The main objective of stirring process is to break the air bubbles and makes homogeneous mixture.

2.3 Tribology Test

Friction and wear test on the prepared samples of SU-8 & its composites were performed on ball-on-disk setup available in Indian Institute of Technology Kanpur. The schematic of ball-on-disk setup is shown in figure 2. For the measurement of coefficient of friction, the load cell was used which is connected to strain measurement system (SCAD500, Pyrodynamics Ltd., India). The strain measurement system was generated analog signal which is converted into digital signal by Data Acquisition System (Technocomm Instruments Pvt. Ltd, India). The calibrating load cell factor was 0.90 N/mV. For friction and wear test at counterface, Si_3N_4 ball of 4 mm diameter with surface roughness of 5 nm was used.

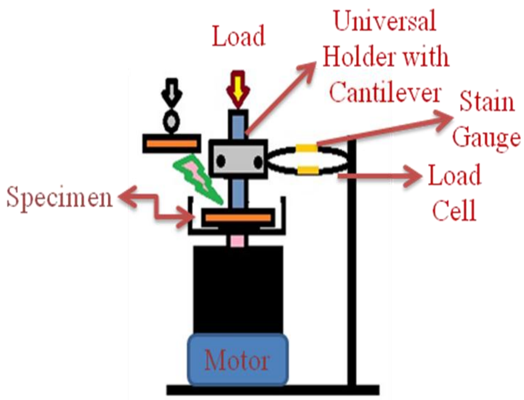

Figure 2: Schematic of Ball-on-Disk Setup

The tribology tests were conducted in atmospheric environment 25 ^{0}Cand 60% relative humidity for 1500 no of cycles at different normal loads available in machine and constant speed (200 rpm) and also different speeds available by controller and constant load (2N). The initial and steady state coefficient of friction will be reported from the sliding tests. The wear life for the tested conditions will be reported as the number of cycles at which the wear track will visible on the substrate with unusually fluctuating friction values. The all tests will be repeated at least 3 times for every sample and average data are reported here.

2.4 Surface Characterization

2.4.1 Optical Microscopy:

The optical microscopy, Eclipse E100 (Nikon Instruments Inc., USA) was used to study the cross-section and surface morphologies of wear track of pure SU-8 and its composite films. For the ball surface study after the tribology test, the Dino-lite (Digital Microscope, Pune, India) was used which is a portable type microscopy of 20 to 250x magnification.

2.4.2 Field Emission Scanning Electron Microscopy (FE-SEM) characterization:

The FE-SEM (∑IGMA, Zeiss, USA) was used to study the cross section and surface morphologies of wear track of pure SU-8 and its composite films. Before FE-SEM imaging, gold coating of thickness 8 nm at 10 mA for 30s was done on every sample using sputter coater (SC7620-CF, Quorum Laughton Lewes). All the images have been taken at 100X magnification which are report here.

2.4.3 Atomic Force Microscopy (AFM) characterization:

The XE7 integrated AFM (Park system, South Korea) system was used for measuring of elastic modulus of SU-8 and it's composite. The test was performed in contact mode using silicon cantilever tip with stiffness of 1.5 N/m.

By using of same system hardness of SU-8 and its composite were measured. Nanoindentation was performed on the sample surface using triangular shape diamond tip. The depth of indentation was given 3000 nm. Our system had capability to nanoindent up to 20 mN loads. At least 8 indents on each sample were taken and reported average values of hardness.

3 Result and Discussion

The film thickness of SU-8 and its composite were formed ~ 35-40 µm on glass substrate and tested under the conditions stated in the experimental procedure section. The following results were obtained and are discussed in the sections below.

3.1 Material

The SEM image of graphene powder is shown in figure 3. From the SEM images, the spherical structure of graphene powder is observed which size is approximately < 100 nm

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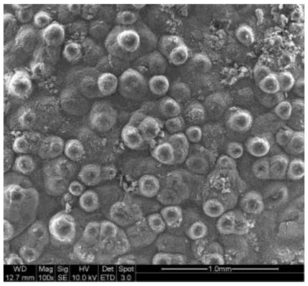


Figure 3: SEM images of Pure Graphene powder. Scale bar 100 µm is given in image.

3.2 Mechanical Properties

Table 1 shows the elastic modulus (E) and hardness of SU-8 and its composites obtained in the nanoindentation testing. The Oliver and Pharr method was used for the calculation of the elastic modulus and hardness. In general, mechanical properties (elastic modulus and hardness) are increased after adding graphene fillers in SU-8. The increase in elastic modulus and hardness is marginally increased.

Table 1: Hardness and Elastic modulus of SU-8 and its composite (5wt %)

Material	Elastic Modulus (GPa)	Hardness (GPa)
SU-8	8.9±2.8	0.729±0.14
SU-8/Graphene	10.49±1.9	0.66±0.13

3.3 Tribology Test

Load Effect on friction:

Figure 4 present the raw data of SU-8 and its composite for 500 numbers of cycles at 1.5 N to 4 N normal load and 50 RPM constant sliding speed. The steady-state coefficient of friction was obtained from average value of the last 100 numbers of

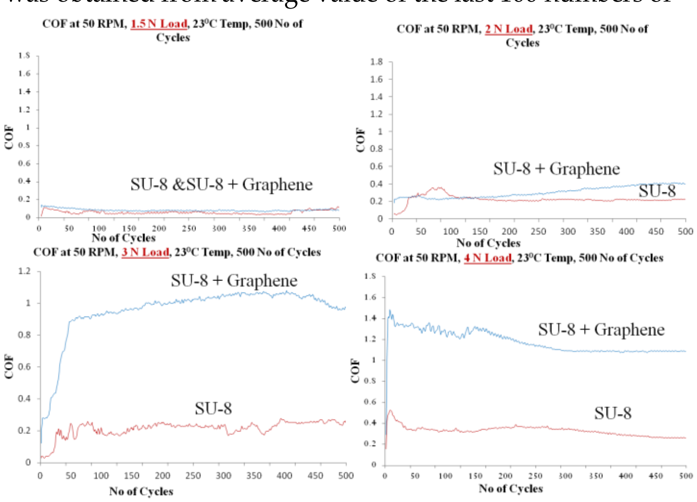
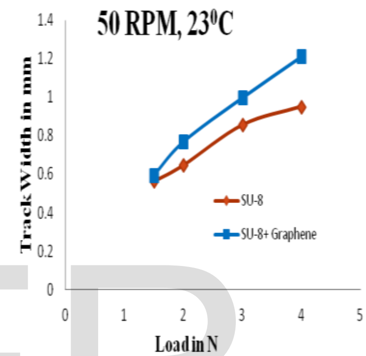


Figure 4: Raw data of coefficient of friction from 1.5 N load to 4 N Load and constant 50 RPM speed for 500 number of cycles cycles, for each test conducted up to 500 cycles. The data for the load effects are summarized in Figure 5 (b). From the figure 4, observed that increase in coefficient of friction with increase in load which is because of the higher contact pressure at interface. At lower load SU-8/graphene (5 wt %) composite gives lower coefficient of friction (~0.15) from pure SU-8.

From the figure 5, (a) graph shows the track width of wear surface after tribology test. From the graph, observed that increase in load increased the track width. Pure SU-8 gives the lower track width at all load from SU-8/graphene composite.

(a)



(b)

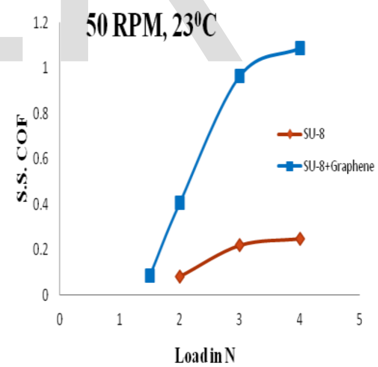


Figure 5: (a): Track width of SU-8 and its composite after tribology test; (b): Steady-state coefficient of friction of SU-8 and its composite after tribology test

After tribology test, the surface is characterized by scanning electron microscopy (SEM). Figure 6 shows the SEM images of SU-8 and SU-8/graphene composite at lower load and maximum load. In both sample at lower load, observed that track width is less but at lower load in case of SU-8/graphene sample, very less amount of material is removed because of the higher contact pressure which produced the heat at interface, heat melt the material at interface which act like a lubricant. This thin film of lubricant reduced the coefficient of friction.

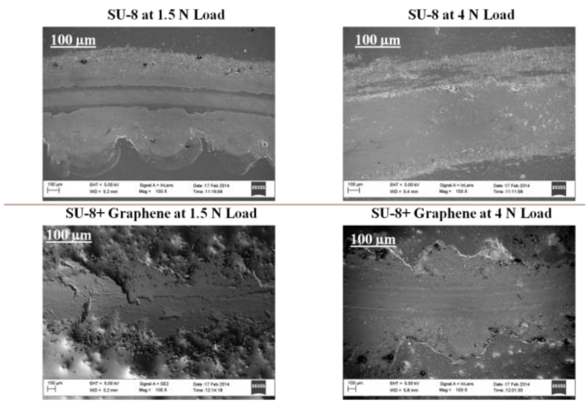


Figure6: SEM image of SU-8 and its composite after tribology test

Speed Effect on Friction:

Figure 7 present the raw data of SU-8 and it's composite for 500 numbers of cycles at 50 RPM to 600 RPM sliding speed and 3 N constant loads. The steady-state coefficient of friction was obtained from average value of the last 100 numbers of cycles, for each test conducted up to 500 cycles. The data for the speed effects are summarized in Figure 17 right side. From the figure, observed that increase in speed reduce the coefficient of friction which is because of heating effect. The heat is generated at counterface more at higher speed because of the higher contact pressure.

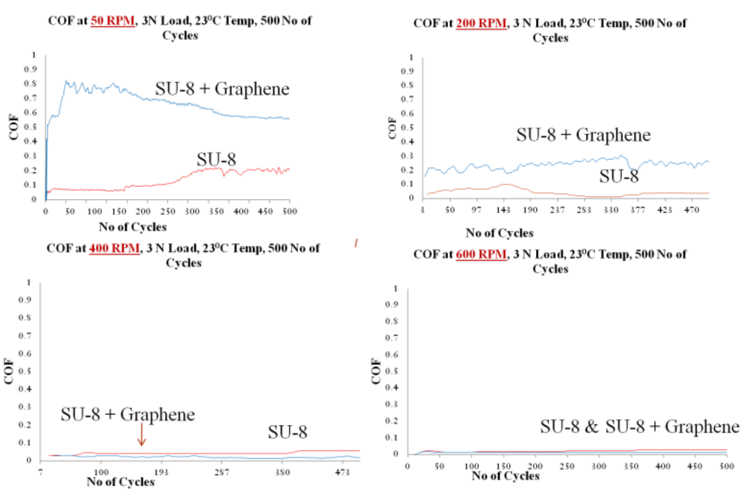
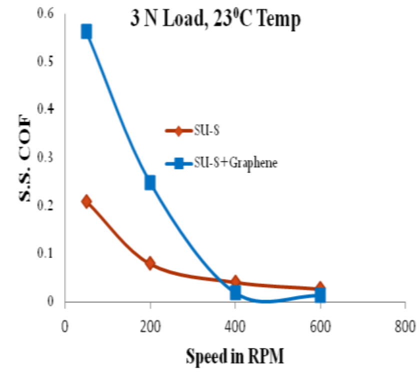


Figure7: Raw data of coefficient of friction from 50 RPM sliding speed to 600 RPM sliding speed and constant 3 N Load for 500 number of cycles

From the figure 8, (a) shown that wear track after tribology test is reduced by increasing the speed from 50 RPM to 600 RPM which shows that the wear is less in both SU-8 and SU-8/graphene composite at higher speed. From figure 8, (b) graph, shown that at lower speed the steady-state coefficient of friction has been higher because of surface roughness and lower contact pressure at counter face.

(a)



(b)

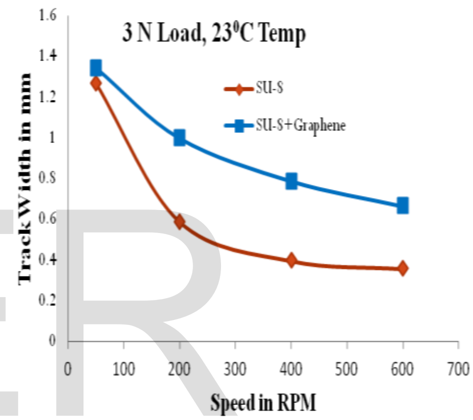


Figure 8: (a): Track width of SU-8 and its composite after tribology test; (b): Steady-state coefficient of friction of SU-8 and its composite after tribology test

After tribology at different speed and constant load, surface is characterized by SEM which is shown in figure 9. The SEM images shown that at higher speed very less wear occurs in SU-8/graphene composite because of interface heating which melt the material at interface and acts as lubricant reduced the coefficient of friction.

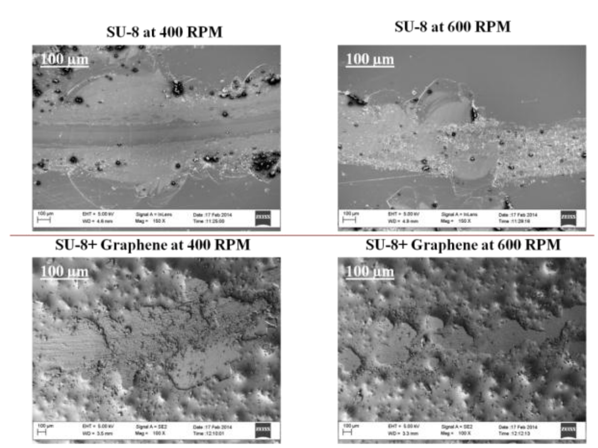


Figure9: SEM image of SU-8 and its composite after tribology test

4 Conclusion

In summary, we have developed the composites of powder 5 weight percentage (graphene) and were conducted surface characterization and tribology test. The major conclusion drawn from this work is listed below:

1. The Coefficient of friction is much higher by adding the Graphene but wear is low.
2. Speed Effect:
   a. At higher Speed the steady state coefficient of friction is low because of frictional heating between the contacts.
   b. At higher speed pressure between the contacts is low in SU-8+ Graphene as comparison to SU-8.
3. Load Effect:
   a. At higher load contact pressure is low by which wear & coefficient of friction is high.
   b. If Load is increases then coefficient of friction is also increases.

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