Role of Graphene oxide and addition of MoS₂ in HDPE matrix for improved tribological properties

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Abstract: The nano filler addition further enhances the properties; especially wear and grating which are very well known. Keeping these points in view, the current work focuses on establishing the tribological behaviour i.e., both slide wear and friction with various load applications for different levels of graphene oxide addition (0.5% to 2%) and MoS₂ addition at 0.8%. The specimens were developed through compression molding technique. The test samples were prepared to the required sizes and subjected to slide wear and friction measurements using pin on disc set up; which is carried out as per ASTM guidelines. The weight change measurements were done by noting the initial and final weight of the test samples to get the slide wear loss. The hardness esteem were obtained by utilizing Shore D Hardness analyzer according to ASTM guidelines. The weight change measurements to get slide wear loses were done. The coefficient of friction was computed by dividing frictional load with normal load. It is very well seen from the test data that the slide wear resistance increments with increment in graphene oxide content (0.5% to 2%) in steps of 0.5%; as the hardness level showed an increase with a similar level of increment in graphene oxide content. The co-efficient of friction has demonstrated a declining pattern with increment in graphene content for the load applications of various loads. The slide wear and friction results have been interpreted based on logical thinking involving literature reports and supporting tests. Thus, there are positive responses observed in respect of the graphene oxide addition to HDPE matrix. This makes the material suitable for wear resistant applications in automotive industries.

1. Introduction

The synthesis of nano particles has gained momentum in recent times from the point of utilizing in different materials like polymers ceramics and composites. In this context, the deployment of graphene and graphene oxide in any matrix has yielded very good results like enhanced mechanical and tribological properties [1]. The oxidizing agents are used to oxidize graphite thereby oxygenated functionalities are introduced in the graphene, thus producing nano layers or few layers of oxygen functionalized graphene known as graphene oxide. Graphene oxide as a filler material in any polymer or ceramic matrix has been proved to be highly successful from the point of achieving very good mechanical, thermal, tribological and other properties. There is a sizable improvement reported in the
literature [2] in respect of mechanical strength, slide wear and friction, thermal conductivity, etc. Keeping these aspects in view, a polymer matrix composite development is envisaged in this work with HDPE as the main matrix and graphene oxide with MoS₂ as filler materials for sliding wear applications.

1.1 Graphene and graphene oxide
Graphene is an allotropic form of carbon having two dimensional atomic scale of hexagonal structure. Graphene has several unusual properties such as 200 times stronger than steel, conduct heat and electricity, good wear resistance and hardness. It has tensile strength of about 130GPa with Young’s modulus of 1TPa [3]. The Graphene is relatively brittle with a fracture toughness of about 4MPa√m [4]. This material can go in any other material in right properties so that the tailor made properties could be achieved. The graphitic oxide or graphite oxide compound of carbon, oxygen and hydrogen in different ratios produced by oxidizing graphite, which is layer structured. The dispersion on the bulk material pertaining to this give rise to nano molecular sheets, which is called as graphene oxide. This material is highly useful in preparing strong paper like materials such as membranes, thin films; composite materials etc. This material serves as an intermediate one to produce graphene by reduction process. The graphene oxide has specific surface properties and found suitable for surfactant applications [5]. In the emulsion system, the graphene oxide gets into the interface between the phases [6]. It is reported in the literature [7], that the adoption of graphene and graphene oxide have resulted in much improved mechanical, electronic, electrical characteristics with a very bright outlook for certain specific applications.

1.2 HDPE matrix and MoS₂
High Density Polyethylene (HDPE) is an organic material in the thermoplastic category. This is produced from petroleum product and finds extensive applications in producing plastic bottles, pipings, membranes, fuel tanks, tubes etc. It is possessing very decent strength to weight ratio with the density ranging from 930 to 970 kg/m³. It can be used upto 120°C for a short time, opaque in nature, possessing tensile strength of about 30 to 32Mpa and resistant to solvents. Molybdenum disulphide (MoS₂) is an inorganic compound consisting of Molybdenum and Sulphur. It is non-reactive, used as a solid lubricant in many engineering applications wherein, it is looked for low coefficient of friction. The low co-efficient of friction is attributed to the weak Vander Waals forces acting between the sulphide atoms.

2.0 Materials and Methods
2.1 Materials
The polymer matrix and filler additions used are detailed in Table 1. Further five different compositions employed in the present work have been designated in the same table.

| Sl. No. | Sample Designation/Code | Test Sample Description |
|---------|-------------------------|-------------------------|
| 1       | HDPE                    | HDPE                    |
| 2       | HDPE (0.5+0.8)          | Filler Wt. (%)          |
| 3       | HDPE (1.0+0.8)          | Graphene Oxide          |
| 4       | HDPE (1.5+0.8)          | MoS₂                    |
| 5       | HDPE (2.0+0.8)          | 0.8                     |

2.2 Methods
The test samples were prepared by adopting the procedures of Brabending and Compression Moulding Technique (CMT). A brief procedure in respect of Brabending and Compression
moulding methods are as discussed. The Brabender basically operates on the feed system in the form of drive units as it provides the drive motor for the processing of modules and contains direct torque measurement system. Initially the temperature and the rotation speed for mixing is set. Raw materials in the form of granules is poured into the mixing attachment; placed between the two rotating rotors. Then; the obtained material is sent for further processing via Compression molding technique. Compression moulding is a notable technique used to develop and manufacture variety of various composites. It is a closed moulding process involving high pressure application. A couple of matched metal molds are used to fabricate composites. In compression molder, base plate is fixed while upper plate is made to easily move. Metallic mold accommodates the reinforcement and matrix; is set in the metallic form and the entire gathering is set in the middle of the pressure disintegrate. Useful utilization of Heat and weight is as per the standard requirements of composite for a specified period of time. By the use of weight and heat, the material set in the middle of the embellishment plates; stream and secures the state of the shape pit giving a high dimensional precision. This depends upon shape outline. Composite curing can be undertaken at room temperature or elevated temperature. Finally after curing, mold is opened and composite product is removed. If, required for uniqueness it is sent for secondary processing. Fundamental rule of a pressure forming machine is; goes about as a press which is arranged vertically with two embellishment parts (best and base halves). In Compression shaping, by and large hydraulic driven component provides path for weight application.

2.2.1. Slide wear and friction
Dry sliding wear tests were performed using Pin-on-disk apparatus, as per ASTM G99-95 standards. All the tests were conducted with test duration of 10 min and adopted a varying load from 40N to 70N with a sliding velocity from 0.44m/s to 0.78m/s. Wear loss was measured in the steady state regime using linear variable differential transducer (LVDT) of accuracy 1μm at the end of 10 min. The wear rates were calculated from height loss data.

2.2.2 Hardness test
Durometer is one of the instruments used to measure the hardness of a material. There are several scales of durometer, used for materials with different properties. The two most common scales using slightly different measurement systems - are the ASTM D2240 Type A and Type D scales. Type D scale is used to measure the Hardness in the present assessment as per the standards used for testing polymers.

3.0 Results and Discussion
The hardness (Shore D) values, slide wear and coefficient of friction data are shown in fig. 1, 2 & 3 respectively.

Fig. 1 Shows Hardness vs HDPE and Polymer Composite Samples
A maximum improvement of 7% is observed for HDPE (2.0+0.8) polymer composites when compared with HDPE for 0.5% graphene addition and the base material.

![Graph showing wear rate vs load for HDPE samples.](image)

**Fig. 2** Shows Wear Rate v/s Load for HDPE Samples

At a maximum load of 70N, a reduction of 40% in the wear rates for HDPE (2.0+0.8) composites when compared with HDPE for 0.5% graphene addition and compared to base material.

A maximum improvement of 17% is observed for HDPE (2.0+0.8) composites when compared with HDPE for 0.5% graphene addition when compared to base material with load 70N.

![Graph showing coefficient of friction vs load for HDPE samples.](image)

**Fig. 3** Shows Coefficient of Friction v/s Load for HDPE Samples

The worn surface features of the test samples using scanning electron microscope (SEM) pertaining to HDPE, HDPE (0.5+0.8), HDPE (1.0+0.8), HDPE (1.5+0.8) and HDPE (2.0+0.8) are shown in figures 4 to 8 respectively at a magnification of 250x. The input parameters employed for SEM examinations are 70N load, 2.4m/s sliding speed, sliding distance of 1445 m. The counter surface being EN31 is an alloy steel of HRC 62 in the heat treated condition. The surface roughness of the counter surface is about 1 µm.
As regards the trend in hardness level for the samples tested, it is very evident from fig. 1 that
the increase in graphene oxide content from 0.5 to 2%, the value increases almost linearly. This is on
the normal line the presentation of any oxide into the framework brings about increment in hardness
[8]. Thus there is coordinated correspondence between the writing report and the present work on
hardness. The information on slide wear misfortune got for the graphene oxide based HDPE
composite demonstrates that it increments with increment in stack (Fig. 2). It is additionally seen from
Fig. 2 that the slide wear misfortune increments with increment in stack application. This is very
consistent since the most noteworthy expansion of graphene oxide in the polymer grid has
demonstrated the best hardness and for the unadulterated HDPE it has demonstrated the minimum.
The SEM pictures likewise bolster these discoveries on wear misfortune information. The
Fig. 4 pertaining to test sample HDPE is showing higher matrix damage, increased debris formation
and a few visible cracks compared to the test samples HDPE 2.0+0.8 (Fig. 8) which is displaying
lesser matrix distortion, lesser debris and less cracks. The other test samples HDPE (0.5+0.8), HDPE
(1.0+0.8), HDPE (1.5+0.8) are showing worn surface features of intermediate in nature. In this
manner, there is balanced correspondence between the SEM highlights and slide wear information, in
this way complimenting each other. Consequently SEM offers confidence to the slide wear information. The work announced by different scientists [9, 10, 11] with the utilization of graphene oxide or some other oxides uncover that the expansion to a lattice enhances the slide wear protection because of the expansion in hardness level contrasted with the oxide free framework. The coefficient of erosion is another parameter which has been resolved for expansion of graphene oxide at four levels (0.5, 1.0, 1.5 and 2.0%) and MoS$_2$ at 0.8% to HDPE lattice. From Fig.3 it is exceptionally well observed that COF diminishes with increment in stack for every one of the examples including unadulterated HDPE test. The most elevated COF is observed to be for unadulterated HDPE and least for HDPE (2.0+0.8) regardless of the heap application (40, 50, 60, 70N).The decrease in COF may be attributed to addition of solid lubricant MoS$_2$ and also the graphene oxide being a good lubricant. The increase in graphene oxide addition has shown decrease in COF. Similarly work reported by other [12] have shown similar trend in COF data. The graphene oxide and MoS$_2$ addition have been proved to be beneficial in reducing friction as well as slide wear loss.

Thus for lower wear loss and low friction applications it would be ideal to employ graphene oxide at 2.0% and MoS$_2$ at 0.8 shows that this combination may be tried especially in automobile applications for better field performance.

4. Conclusion

- Hardness of the polymer composite with signature HDPE (2.0+0.8) improved by 7% hinting the active distribution of reinforcement effectively.HDPE (2.0+0.8) composites showed bring down coefficient of rubbing (17%) and bring down wear rate (40%) when contrasted and HDPE under every one of the heaps and sliding speeds considered. Altogether lessened wear rate can be ascribed to the annihilation of the conceivable MML layer shaped and material softening because of expanded temperature with expanded sliding speed amid the sliding process.SEM morphology of the ragged surfaces uncovers that the degree of damage is minimum for HDPE (2.0+0.8) when contrasted with the base material.

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References

[1] Hamed Asgharzadeh, Maryam Sedigh, Synthesis and mechanical properties of Al matrix composites reinforced with few-layer graphene and graphene oxide Journal of Alloys and Compounds 728 (2017) 47-62.
[2]. Yue Chen, Duxin Li, Wenyan Yang, Chunguang Xiao, Enhancement of mechanical, thermal and tribological properties of AAPS-modified graphene oxide/ polyamide 6 nanocomposite, Composites Part B 138 (2018) 55-65
[3] Dimitrios G. Papageorgiou, Ian A. Kinloch, Robert J. Young, Mechanical properties of graphene and graphene-based nano composites Progress in Materials Science 90 (2017) 75–127
[4] G. Rajasekaran , Avinash Parasr; Enhancement of fracture toughness of graphene via crack bridging with stone-thrower-wales defects Diamond & Related Materials 74 (2017) 90–99
[5] Yishan Wang, Shengyi Yang, Haowei Wang, Li Zhang, Haijuan Cheng, Bo He, Weile Li, Bingsuo Zou, Surfactant-treated graphene oxide in organic solvents and its application in photovoltaic cells Current Applied Physics (2017), doi: 10.1016/j.cap.2016.12.017
[6] Oraporn Wong-u-ra, Sanong Ekgasit, Kanet Wongravee, Phase transferring of silver nanoparticles to organic solvents using modified graphene oxide as carrier *Materials Chemistry and Physics* 199 (2017) 348-355

[7] Nam K-H, Im Y-O, Park HJ, Lee H, Park J, Jeong S, Kim SM, You N-H, Choi J-H, Han H, Lee K-H, Ku B-C, Photo acoustic effect on the electrical and mechanical properties of polymer-infiltrated carbon nanotube fiber/graphene oxide composites, *Composites Science and Technology* (2017), doi: 10.1016/j.compsscitech.2017.10.014

[8] F.V. Ferreira, F.S. Brito, W. Franceschi, E.A.N. Simonetti, L.S. Cividanes, M. Chipara, K. Lozano, Functionalized graphene oxide as reinforcement in epoxy based nanocomposites *Surfaces and Interfaces* 10 (2018) 100–109.

[9] Yingfei An, Zhixinn Tai, Yuanyuan Qi, Xingbin Yan, Bin Liu, Qunji Xue, Jinying Pei, Friction and wear properties of graphene oxide/ultrahigh-molecular-weight polyethylene composites under the lubrication of deionized water and normal saline solution, *Journal of Applied Polymer Science*, Volume 131, Issue 1 January 2014

[10] Jianyi Wang, Cheng Peng, Jinzhu Tang, Zhanxin Xie, Friction and wear characteristics of containing a certain amount of graphene oxide (GO) for hot-pressing sintered NiCr-WC-Al2O3 composites at different temperatures, *Journal of Alloys and Compounds* (2018) Vol 737 515-529.

[11] Anshun H, Shuiquan Huang, Jung Ho Yun, Zhengyi Jiang, Jason Stokes, Sihai Jiao, Lianzhou Wang, Han Huang, The pH-dependent structural and tribological behaviour of aqueous graphene oxide suspensions, *Tribology International* (2017) 460-469.

[12] Chih A, Anson-Casaos A, Puertolas JA, Frictional and mechanical behavior of graphene/UHMWPE composite coatings, *Tribology International* (2017), doi: 10.1016/j.triboint.2017.07.027.