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ORIGINAL ARTICLE

Tribological performance of paraffin grease with silica nanoparticles as an additive

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Abstract

The present study deals to evaluate the physical properties, frictional behavior, and extreme pressure performance of paraffin grease dispersed with silica (SiO_2) nanoparticles. The paraffin grease was developed using paraffin oil as a base oil and 12-lithium hydroxy stearate was chosen as a thickener. The concentration of thickener was fixed at 14% w/w. The SiO_2 nanoparticles were synthesized by the modified sol–gel method and dispersed in paraffin grease by the in-situ method. The various analytical tools were used to ensure the formulation of SiO_2 nanoparticles. The extreme pressure and frictional characteristics of SiO_2 doped in paraffin grease were studied in four-ball tester as per ASTM D2596 and D2266, respectively. The physical properties of paraffin greases such as cone penetration, drop point, water washout, leakage tendency, and evaporation loss were also evaluated according to ASTM standards. The experimental results showed that the addition of SiO_2 nanoparticles in paraffin grease enhances its tribological performances as compared to pure paraffin grease. The maximum reduction in coefficient of friction and mean wear volume was ~20% and ~42% at a concentration of 0.03 and 0.05% w/w, respectively.

Keyword Paraffin grease · Nanoparticles · Friction · Wear scar diameter · Sol–gel method.

Introduction

Grease is a semi-solid lubricant consists of lubricating oil, which can be either mineral or synthetic and thickening agent which can be either soap or non-soap. Grease is widely used in various severe operating conditions such as extreme pressure, high speed, and temperature. The performance of grease is mostly affected by the concentration of the thickening agent as well as base oil type and its viscosity. The additives of nano-size are doped into the grease to enhance its tribological performances of the mating surfaces. In recent years, nanoparticles as an additive in the lubricating system have attracted the researchers because of its excellent physical and tribological properties. Different kinds of nanoparticles have been investigated for tribological performances. It has been reported that nanoparticles such as metal oxides (ZrO_2, TiO_2, Fe_3O_4, Al_2O_3, ZnO, CuO, SiO_2), metal (Sn, Fe, Bi, Cu, Ag, Ti, Ni, Co, Pd, Au), and sulfides (WS_2, CuS, MoS_2, $NiMoO_2S_2$) were used as an additive in the lubricants in majority (Dai et al. 2016). Among the reported nanoparticles, SiO_2 nanoparticles are one of the best candidates for tribological applications. The effectiveness of nanoparticles is dependent on the size, morphology, roughness, and compatibility with base oil. There has been growing interest to facilitate satisfactory dispersion of nanoparticles in lubricants, where in which dispersants or surface modification of nanoparticles has been employed (Li and Zhu 2003; Li et al. 2006; Sui et al. 2015a, b, 2016). In the past decade, hybrid/composite nanoparticles were incorporated as an additive in the base lubricating oil to augment tribological performance (Jiao et al. 2011; Li et al. 2011; Kim et al. 2011; Zhang et al. 2012). Tribological performance of SiO_2 nanoparticles has been explored as a lubricant additive in oil/grease products (Peng et al. 2009; Chen 2010; Ge et al. 2015; Xie et al. 2016).

Xie et al. (2016) have evaluated the effect of SiO_2 and MoS_2 nanoparticles on the tribological behavior of the engine oil (EOT5). They reported the effect of nanoparticle concentration on load-bearing capacity and the stability of the lubrication film. Furthermore, it was observed that MoS_2 in lubricants had a pronounced influence on the load-bearing capacity and lubrication film stability as compared

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to SiO_2 nanolubricants. Peng et al. (2009) have demonstrated that the surface-modified diamond (0.2–0.5 wt%) and SiO_2 (0.1–1.0 wt%) with oleic acid have enhanced the tribological properties of liquid paraffin in terms of load-bearing capacity, antiwear, and friction properties. Furthermore, Peng et al. (2010) have investigated the size effects of SiO_2 nanoparticles as an additive on the tribological performance of paraffin oil, and their results showed that surface-modified SiO_2 nanoparticles with oleic acid having a diameter of 58 nm have improved the tribological behavior of the liquid paraffin. The distilled water containing 1.0% of Cu nanocrystals encapsulated with silica (i.e., nanocomposite) as an additive can significantly improve the antiwear and load-carrying capacity (Zhang et al. 2012). The 0.5 wt% concentration of alumina/silica composite nanoparticles was effectively improved the tribological performance of lubricating oil (Jiao et al. 2011). Chen (2010) has studied the tribological behavior of titanium complex greases containing nano-TiO_2 and SiO_2 as an additive, and results showed an excellent friction reduction, antiwear properties, however, and no effect on the load-bearing capacity. Ge et al. (2015) have evaluated the insulation effect and tribological performance of the transformer oil-based grease with nano-TiO_2 and SiO_2 as an additive. It was observed that grease doped with 0.1 wt% of the additive had enhanced alternating current breakdown strength, power frequency by 10.4 and 8.2%, respectively. Antiwear test results showed that nano-TiO_2 grease has excellent tribological characteristics, while nano-SiO_2 grease displayed good friction reducing characteristic.

From the above, it is clear that nano-SiO_2 has a significant potential to enhance the tribological characteristics of lubricating oil and grease. Furthermore, it has been found that the tribological performance of SiO_2 nanoparticles of various sizes was doped in the commercially available lithium grease. It is important to note that commercially available grease contains a variety of additives and fillers to surplus its properties. It is difficult to ascertain the actual behavior of nanoparticles on a lubrication behavior when the grease was already doped with different additives. In view of the above, the objective of this work was to evaluate the tribological performance of paraffin grease with SiO_2 nanoparticles as an additive. The SiO_2 nanoparticles were synthesized by the modified sol–gel technique. The SiO_2 nanoparticles were dispersed in paraffin grease in a very low concentration in the range between 0.01 and 0.05% w/w by the in-situ method. The antiwear and extreme pressure properties have been investigated in four-ball tester as per ASTM standards. The paraffin grease without adding additives was used as a standard to compare the various physical and tribological performances of SiO_2-doped paraffin grease. In addition, another aim of this work was to investigate the optimal concentration of nanoparticles in the paraffin grease for finding the best tribological performance.

Experiment details

Synthesis of SiO_2 nanoparticles

The modified sol–gel method was used for the synthesis of SiO_2 nanoparticles. The SiO_2 nanoparticles were synthesized according to the procedure reported by Jafarzadeh et al. (2009). Tetraethoxysilane TEOS (> 96.0%, TCI), ethanol (99.9%, ACS Reagent), NH_3 (28–30%, ACS) chemical reagents, and distilled water were used in the synthesis of SiO_2 nanoparticles. In a typical procedure, 10 mL of TEOS was first dissolved thoroughly in 60 mL of ethanol. The reaction solution was positioned under the low-frequency ultrasonic machine (GT SONIC, GT-1730QTS, China) at a temperature less than 30 °C for 10 min. For hydrolysis of TEOS in the ultrasonic bath, 2 mL of distilled water was added in dropwise in the reaction mixture by maintaining the feed rate of 0.2 mL/min. After 1.5 h, 4 mL of NH_3 (catalyst) was added dropwise in the reaction mixture with the feed rate of 0.05 mL/min. The sonication was continued for 3 h followed by gelation for 1 h. The gel was washed with a mixture of 1:1 (v/v) ratio of ethanol and distilled water. The reaction mixture was white in color was centrifuged three or four times at 6000 rpm for 15 min. The suspension was washed with acetone to remove the traces of impurities and dried in a conventional oven at 70 °C for 24 h. Figure 1 shows the flow chart for the synthesis of silica nanoparticles. The nanoparticles were produced at laboratory scale. The yield of each batch was calculated as reported by Rahaman et al. (2007). The modified sol–gel technique showed a yield of ~ 70% of nano-SiO_2. The yielding of silica and size of nanoparticles was depended upon the feed rate of ammonia, operating temperature, and the concentration of the reactants. The various analytical tools were used to ensure the formulation of SiO_2 nanoparticles. X-ray diffractometer (XRD, Rigaku, Miniflex 600 D/teX Ultra, Cu K radiation, USA) was used to characterize the phases of synthesized SiO_2 nanoparticles at diffraction angle ranging from 10 to 80°. Fourier-transform infrared spectroscopy (FTIR, Bruker ALPHA ECO-ATR, MA furnished with ZnSe ATR crystal with a scan rate of 24 at a resolution of 2 cm^{-1}) analysis was carried out to monitor chemical functionalization of silica nanoparticles in a spectrum ranging between 500 and 4000 cm^{-1}. High-resolution scanning electron microscopy HR-SEM (FEI, NOVA NANOSEM 450, USA) was used to study the shape and size of the nanoparticles.

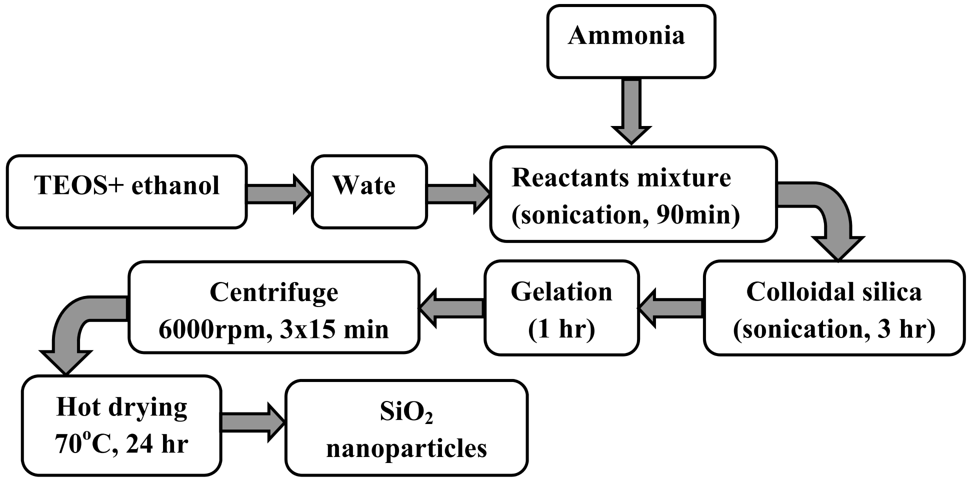

Fig. 1 Flow chart for the synthesis of silica nanoparticles

Formulation of paraffin grease with SiO_2 nanoparticles

The various procedures were reported for the formulation of grease by the several researchers (Adhvaryu et al. 2005; Delgado et al. 2005; Wang et al. 2008). In the present study, the grease was synthesized with paraffin oil (s–d fine-chem) as a base oil and 12-lithium hydroxy stearate metal soap as a thickening agent. Paraffin oil has a kinematic viscosity of 64cP, at 37.8 °C. In the previously reported literature, the nanoparticles were doped in the grease after the formulation of the grease (Chen 2010; Wang et al. 2008). The dispersion of nanoparticles in the grease may not be effective because of a heterogeneous mixture. In the present study, the nanoparticles were dispersed in the base oil to ensure homogeneous dispersion in the grease. The SiO_2 nanoparticles were dispersed into the base oil at different concentrations in the range between 0.01 and 0.05% w/w. The grease was prepared by in-situ saponification reaction between a 12-hydroxy steric acid (> 80%, TCI) and lithium hydroxide monohydrate (99%, Spectrochem). A measured quantity of nanoparticles was dispersed into the paraffin oil using a magnetic stirrer (IKA, C-MAG HS4 digital, Germany) at room temperature for 30 min. For the homogenous dispersion of nanoparticles in the oil, the mixture was kept in water bath sonication (GT SONIC, GT-1730QTS, China) at room temperature for 1 h. Overhead mechanical stirrer (REMI ELEKTROTECHNIK LTD, RQT-124A, India) appended with square edged anchor impeller was used to stirrer the solution. 12-hydroxystearic acid was added slowly into the mixture and stirred continuously at 200 ± 10 rpm and heated at 90 ± 2 °C. In parallel, lithium hydroxide monohydrate was dissolved homogeneously in distilled water and added dropwise to the mixture as soon as 12-hydroxystearic acid started to melt, and a waxy transformation takes place. The mixture was allowed to stir at 300 ± 10 rpm at a temperature of 180 ± 2 °C for 2 h, followed by cooling at room temperature for 24 h.

Physical and tribological characterization of grease

The physical properties of synthesized paraffin grease were measured in accordance with ASTM standards (Table 1). The properties measured are cone penetration (unworked/worked grease) (Khusboo Sci. Pvt. Ltd., Mumbai, India), drop point (Wadegati labequip Pvt. Ltd, WIL-565, Mumbai, India), water washout [Stanhope Seta, Seta, 1961 (Mark II), UK], leakage tendency (Stanhope Seta, 1900, UK), evaporation loss (Khusboo Sci. Pvt. Ltd., Mumbai, India). Cone

Table 1 Test conditions used for physical characterization of paraffin grease

Physical characterization	ASTM standard	Duration (min)	Quantity of grease required (gm)	rpm	Temperature (°C)	Flow rate (ml/sec)	Heat rate (°C/min)
Cone penetration	D 1403	0.0833	10	–	25	–	–
Drop point	D 566	Not defined	2	–	− 5 to + 300	–	4–7
Water washout	D 1264	60	4	600	79	5 (water)	–
Leakage tendency	D 1263	360	90	660	105	–	–
Evaporation loss	D 972	1320	20	–	100	33.333 (air)	–

penetration test indicates the consistency of the grease. The detailed test conditions adopted for the physical characterization of synthesized paraffin grease is tabulated in Table 1. The mass loss of paraffin grease with temperature was recorded using a thermal gravimetric analyzer (TGA, PerkinElmer, Diamond, US) in the temperature range between 45 and 800 °C with the thermal rate of 10 °C.min^{-1} under a steady flow of nitrogen gas.

Four-ball tester (DUCOM Instruments Pvt. Ltd., TR-30H-KRL-RFA, India) was used for the evaluation of the tribological behavior of paraffin greases. The antiwear and extreme pressure properties were evaluated as per ASTM D2266 and D2596, respectively. Test balls are made of chrome alloy steel (AISI-52100) in a diameter of 12.7 mm. The hardness of steel balls was in the range between 59 and 61 HRC. Before the beginning of the test, steel balls, ball pot, collet, and splash guard were cleaned with acetone in a sonicator for 20 min. In a ball pot, three stationary clamped steel balls were filled with grease and ensured that no air bubbles are entrapped, and the top surface was covered. In the antiwear test, top ball fixed in the collet and applied a force of 392N on the three balls for point contact. The test samples were maintained at a temperature of 75 °C, and then, the top ball was rotated at 1200 rpm for 1 h. The extreme pressure test was performed to determine the load-bearing capacity of the grease, i.e., weld point and the last non-seizure load. This test was conducted at different loads as per the ASTM standard with the rotating speed of the spindle of 1760 ± 40 rpm at room temperature of 27 ± 8 °C. Each test was performed with fresh samples for three times to find the repeatability. The schematic diagram of the four-ball tester is shown in Fig. 2.

After each test, the wear scar diameter of the steel balls was measured using image acquisition. The scanning electron microscope (SEM, Zeiss EVO 18 Research, Germany) was used to understand the wear patterns of the worn surfaces. Furthermore, energy-dispersive spectroscopy (EDS) analysis of the worn surfaces was carried out to know the elemental distribution. The arithmetical mean surface roughness and the root-mean-square surface roughness of the worn surfaces were measured with a contact mode atomic force microscopy (AFM, BT 02218 Nanosurfeasyscan 2 basic AFM, Switzerland).

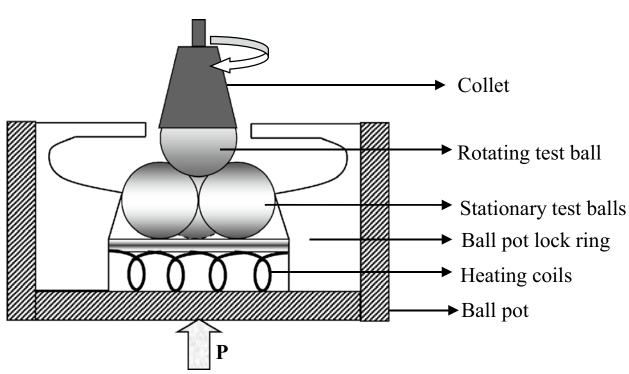

Fig. 2 Schematic diagram of four-ball test arrangement

Results and discussion

Characterization of SiO_2 nanoparticles

The particle size and morphology of SiO_2 nanoparticles were characterized using HR-SEM. The shape of SiO_2 nanoparticles is almost spherical which is depicted in Fig. 3a, b. IMAGE J software was used for the measurement of the size of the nanoparticles. The variation in the size of nanoparticles is shown in Fig. 3c. The average particle size was found to be ~ 70 nm and size distribution was in the range between ~ 40 and 113 nm. Figure 3d indicates that the frequency distribution of particles and the majority of nanoparticles were lying in the range between 50 and 70 nm. The crystalline and phase identification of nanoparticles were studied using XRD technique. X-ray diffraction pattern of synthesized SiO_2 nanoparticles is shown in Fig. 4a. The single characteristic diffraction peak at ~ 21.24° attributed to 101 plane is fully matched with a JCPDS data card No 89-8951, which affirms the formation of SiO_2 nanoparticles. Figure 4b shows FTIR spectra of SiO_2 nanoparticles. The broad diffraction peak reveals that SiO_2 is amorphous in nature (Lima et al. 2011; Ge et al. 2015). The infrared vibrations of silica show an asymmetrical Si–O–Si stretching in the range between 1250 and 1020 cm^{-1} (Vansant et al. 1995; Rahman et al. 2007; Wang et al. 2010). An intense vibrational peak at ~ 1071 cm^{-1} is noticed due to an asymmetrical Si–O–Si stretching, which is a shred of evidence for the synthesis of SiO_2 nanoparticles. A small peak at ~ 950 cm^{-1} is observed due to Si–O–H bending (Vansant et al. 1995). A hump is marked in the FTIR spectrum in the range between 3100 and 3600 cm^{-1} is present due to the stretching of O–H (Rahman et al. 2007).

Study of physical and tribological performance of paraffin grease

Figure 5 shows a typical image of synthesized paraffin grease dispersed with SiO_2 nanoparticles in the range between 0.01 and 0.05% w/w. There was no change in the color of grease with a change of concentration. The results of cone penetration, dropping point, evaporation loss test, leakage tendency, and water washout are reported in Table 2.

The results showed that the synthesized paraffin greases having the consistency of NLGI 0 grade indicate the semi-solid state. There was no significant difference in the

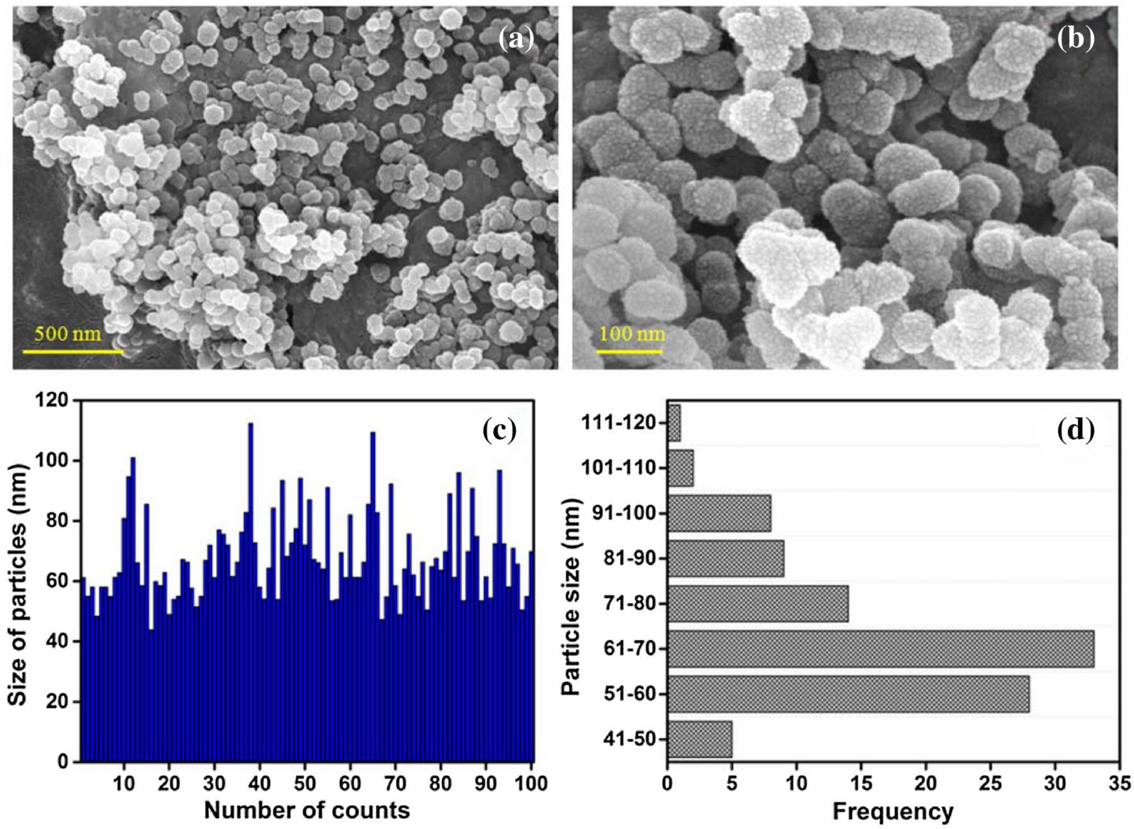

Fig. 3 **a, b** HR-SEM images of SiO_2 nanoparticles, **c** variation in the size of nanoparticles with number of counts, **d** frequency distribution of nanoparticles

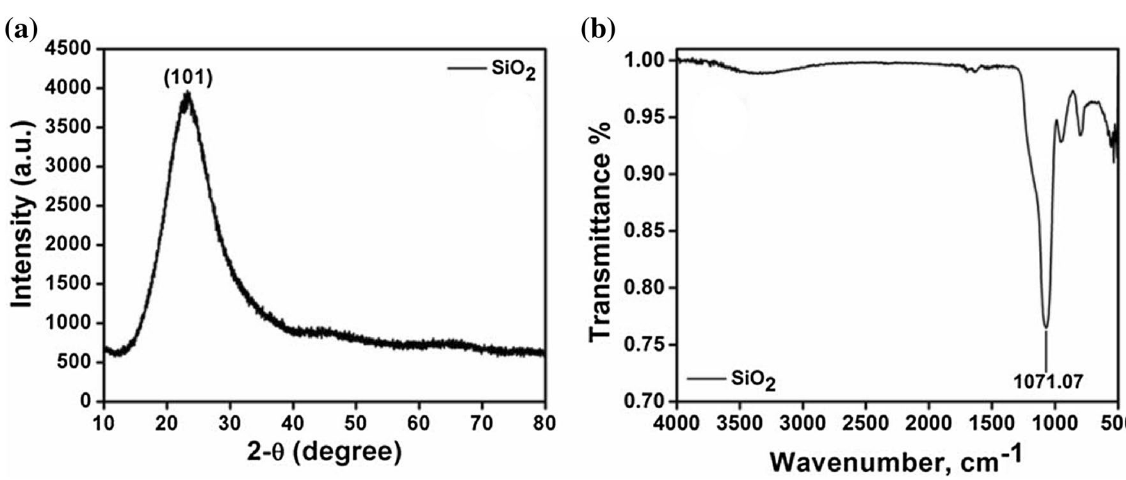

Fig. 4 **a** XRD of SiO_2 nanoparticles, **b** FTIR spectrum of SiO_2 nanoparticles

properties between unworked and worked penetration of paraffin grease and thus indicates its good shear stability. The addition of a small fraction of SiO_2 nanoparticles in paraffin grease does not show any effect on consistency, dropping point, evaporation loss, leakage tendency, and water washout characteristic of the paraffin grease. All tests have been performed with fresh samples three times to maintain the repeatability and the average value was reported. Figure 6 shows thermal gravimetric and derivative function pattern of SiO_2 doped in paraffin grease. TGA curve displayed

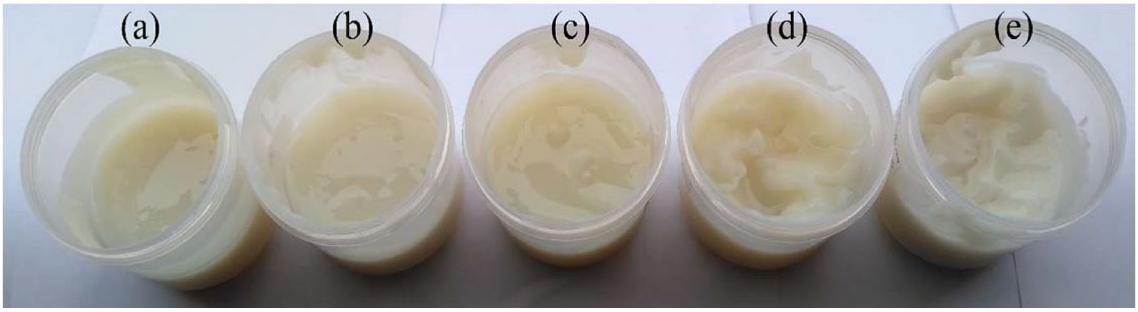

Fig. 5 Paraffin grease with SiO_2 in various concentrations (%): **a** 0.01, **b** 0.02, **c** 0.03, **d** 0.04, **e** 0.05

Table 2 Test results for various physical characterizations of paraffin grease

Tests	Pure paraffin grease		SiO_2 doped paraffin grease	
Cone penetration (1/10 mm)	Unworked penetration	Worked penetration	Unworked penetration	Worked penetration
	358	372	361	377
Drop point (°C)	201		200.5	
Evaporation loss (%)	3.14		3.18	
Leakage loss (%)	26.85		26.40	
Water washout (%)	42.0		41.8	

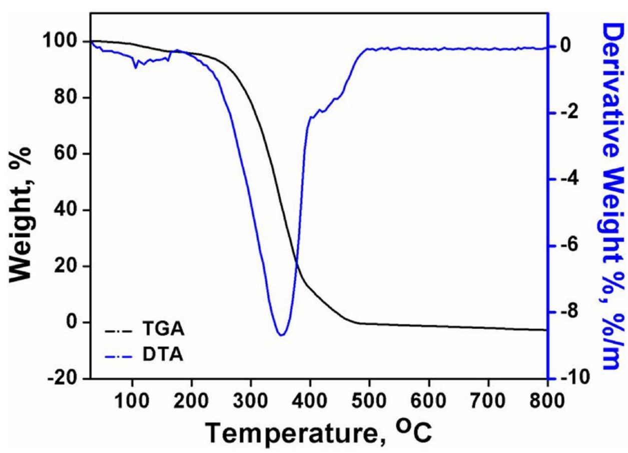

Fig. 6 Thermal degradation pattern of SiO_2 nanoparticle-doped paraffin grease

that there is no early weight loss which indicates that there is an absence of water molecules in the synthesized paraffin grease. Single-stage decomposition indicates the homogeneous structure of the grease (Sánchez et al. 2011). TGA response demonstrated that the highest thermal stability of SiO_2-doped paraffin grease was up to 290 °C and decomposition temperature was in the range between 230 and 400 °C. The TGA response of the synthesized grease is also affected by the volatility of the base oil. The maximum decomposition rate occurs at the temperature of 352 °C which is illustrated by the maximum peak in the DTG curve.

Figure 7a shows a variation of the average coefficient of friction and wear scar diameter with increasing dose of SiO_2 nanoparticles in the paraffin grease. The pure paraffin grease showed the coefficient of friction of 0.09017 which is gradually decreased with increasing concentration of SiO_2 nanoparticles and exhibited a minimum coefficient of friction of 0.07196 at 0.03% w/w doping of nanoparticles. In addition, the increment in the concentration of SiO_2 nanoparticles demonstrated a gradual increase in coefficient of friction. The wear scar diameter on a steel ball with pure paraffin grease was found to be 859.27 µm and decreases gradually with an increase in the concentration of SiO_2 (756.73 µm at 0.05% w/w). Figure 7b shows the variation in the coefficient of friction with time for pure paraffin grease and 0.03% w/w SiO_2 nanoparticle-doped paraffin grease. The friction curve of pure paraffin grease shows a gradual rise and fall in the coefficient of friction with time and attains a constant value. At a concentration of 0.03% w/w of SiO_2, nanoparticles prevent the asperity-to-asperity contact due to which friction coefficient gradually decreased with the time. Figure 7c shows the effect of the doping concentration of SiO_2 nanoparticles on mean wear volume of steel balls. The minimum wear loss was obtained at 0.05% w/w and it is compared with the pure paraffin grease. Figure 7d shows a percentage reduction in wear volume, wear scar diameter, and coefficient of friction with increasing dose of SiO_2 nanoparticles. The maximum decrease in the coefficient of friction was obtained at 0.03% w/w doping of SiO_2 and it is approximately about ~ 20%. The wear scar diameter was

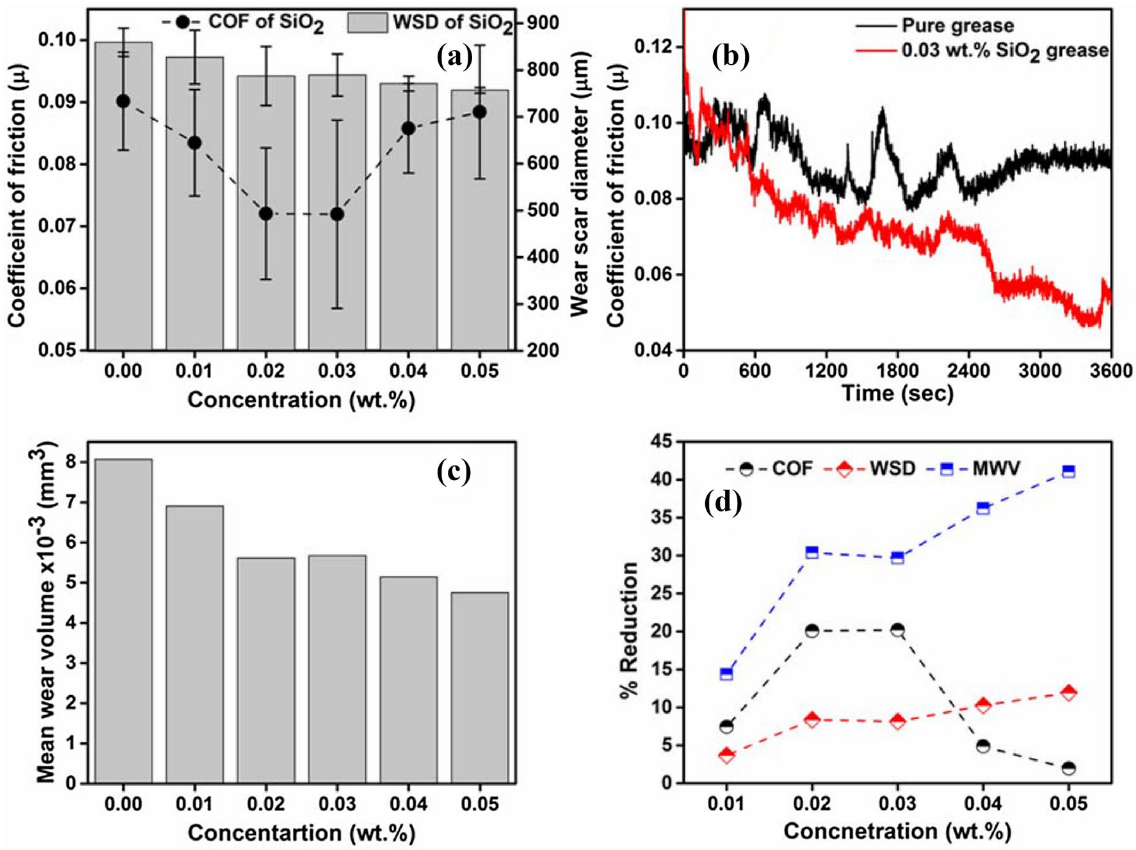

Fig. 7 **a** Variations in the coefficient of friction and wear scar diameter with doping concentration of SiO_2 nanoparticles, **b** variations in the coefficient of friction with time at optimum concentration of SiO_2 nanoparticles, **c** variations of wear volume with doping concentration of SiO_2 nanoparticles, **d** percentage reduction in the wear volume, wear scar diameter and coefficient of friction with variation in concentration of SiO_2 nanoparticles

reduced by ~12%, while mean wear volume was reduced by ~42% at 0.05% w/w. The following aspect can explain the improvement in the tribological behavior of paraffin grease by dosing of SiO_2 nanoparticles. The morphology and size of SiO_2 nanoparticles play an important role in the enhancement of tribological performance. Figure 3a, b shows HR-SEM images of SiO_2 nanoparticles, which are almost spherical. Dai et al. (2016) have reviewed and found that spherical morphology showed spectacular tribological behavior than other morphologies. Spherical shape facilitates for rolling which minimize asperity-to-asperity contact between the rubbing surfaces (Chang et al. 2014; Ge et al. 2015; Kashyap and Harsha 2016; Gupta and Harsha 2017). Spherical nanoparticles behave as nano-bearing due to this sliding friction is converted into rolling friction by nanoparticles at the rubbing surfaces. This phenomenon reduces shear stress, which assisted in the reduction of the coefficient of friction and material removal.

Extreme pressure property of pure and SiO_2 blended paraffin grease was examined as per the ASTM standard in four-ball tester. This test was performed to determine the load-bearing capacity of the lubricating grease. Extreme pressure test result unveiled the effect on the load-bearing capacity of paraffin grease with the addition of SiO_2 nanoparticles. Test results of extreme pressure showed that the last non-seizure and weld loads for both pure and SiO_2-doped paraffin grease were 126 and 160 kgf, respectively. The test result shows that there was no change in the load-bearing capacity of paraffin grease with the addition of a very small fraction of SiO_2 nanoparticles as an additive. The SiO_2 nanoparticles were subjected to Hertzian contact stress of 7.37 GPa for a given load. Therefore, at this Hertzian contact stresses, a very small fraction of SiO_2 nanoparticles in the paraffin grease will squeeze out and not able to provide load-bearing ability to the grease. Similar to the present test results, Chen (2010) has also reported no improvement in the load-bearing capacity with the addition of 1.5 wt% nano-SiO_2 in the titanium complex grease.

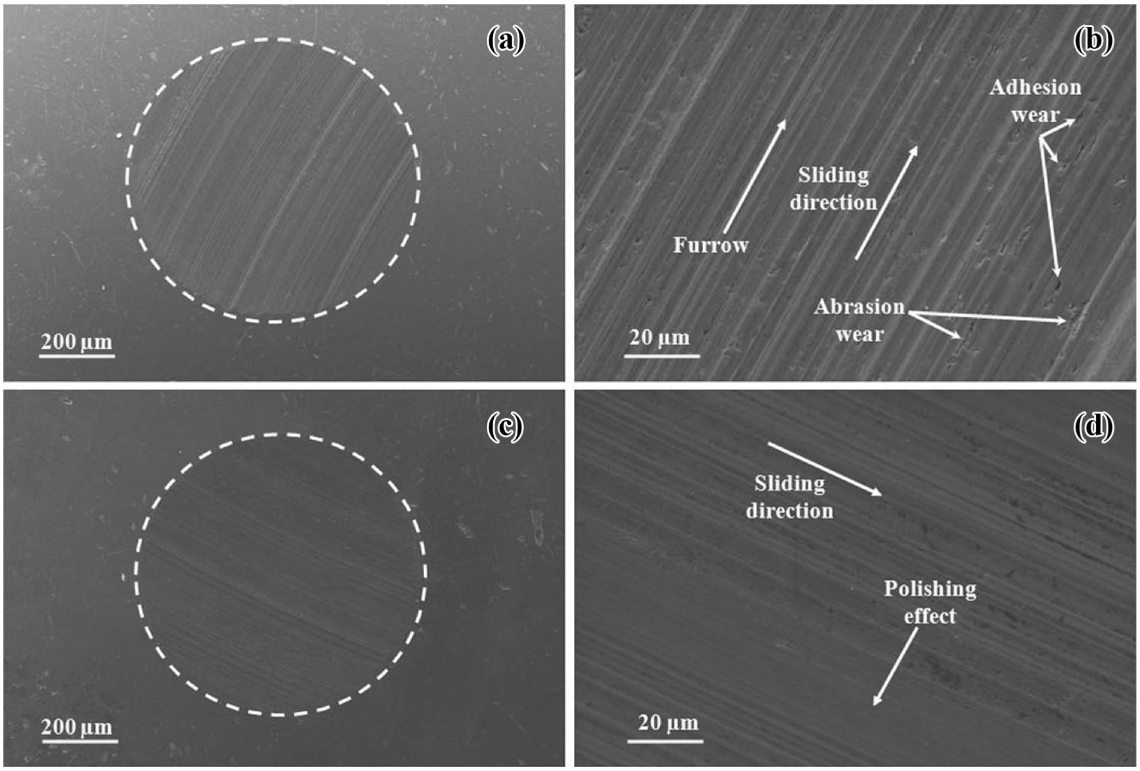

Fig. 8 SEM of worn surfaces of steel balls lubricated by: **a, b** pure paraffin grease, **c, d** SiO_2 doped paraffin grease

Study of worn surfaces

Figure 8a–d shows the SEM images of a worn steel ball of pure and SiO_2-doped grease. The worn surface indicated a typical feature of furrows in the direction of sliding. In Fig. 8b, pits are visible on the worn surface, and this is a clear indication of material removal by adhesion and abrasion wear mechanism. On the other hand, worn surface lubricated with SiO_2-doped paraffin grease showed a smooth appearance and lesser furrows, and this is due to the better separation of the mating surfaces. High-specific surface area and small size of nanoparticles help them to accommodate easily between the tribo-pairs and repairs the surface by mending effect (Liu et al. 2004; Gupta and Harsha 2018). Figure 9 shows the schematic of lubrication mechanism of the grease along with nanoparticles. The real area of contact of the friction surfaces has been increased due to the presence of nanoparticles, which has contributed to a decrease in the contact pressure. Nanoparticles as well as grease fill the dimples and valleys of the surfaces and form a protective

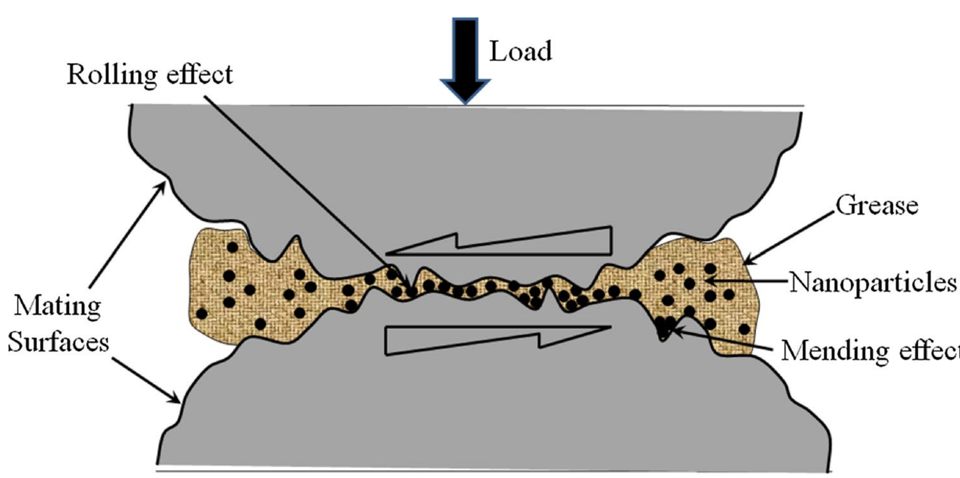

Fig. 9 Schematic of lubrication mechanism in the grease along with nanoparticles

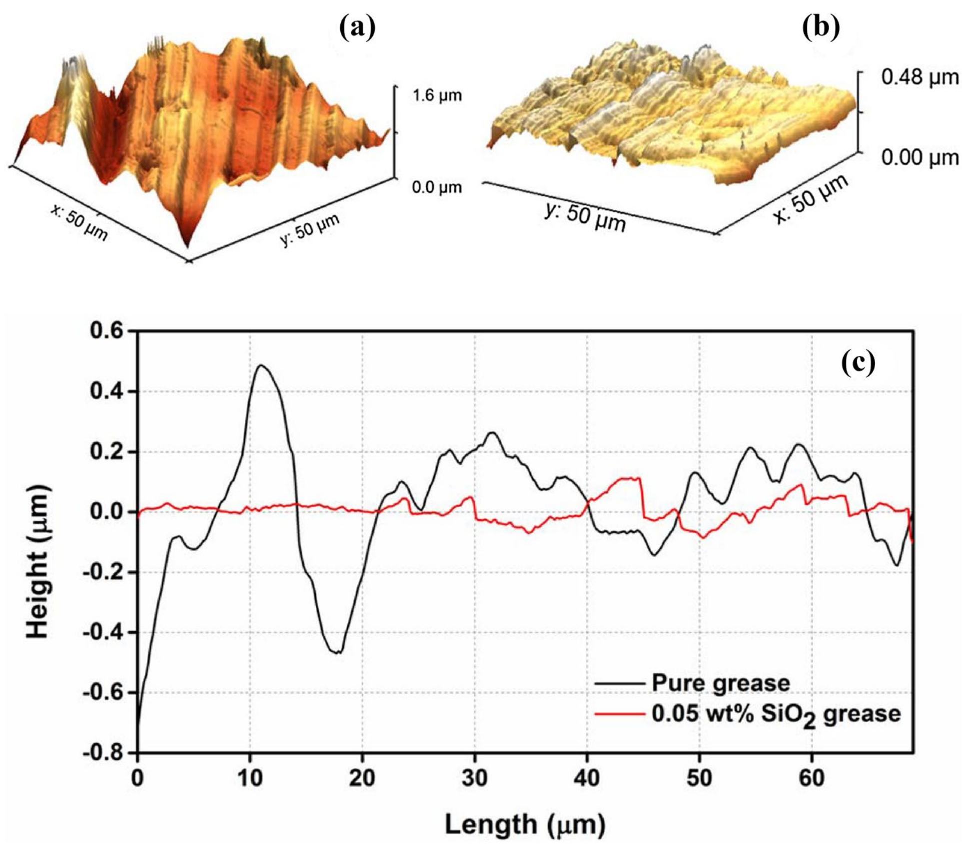

Fig. 10 AFM 3D view of worn surface lubricated by: **a** pure paraffin grease, **b** 0.05 wt% SiO_2 grease, **c** line profile of worn surfaces of both grease

Table 3 Surface roughness of worn steel ball surfaces

Grease	Line roughness		Surface roughness	
	Ra (in µm)	Rq (in µm)	Sa (in µm)	Sq (in µm)
Pure grease	0.266	0.339	0.266	0.335
SiO_2 doped grease	0.0251	0.0307	0.0216	0.0272

layer which protects the direct contact of the tribo interfaces (Chang et al. 2014; Gupta and Harsha 2017).

Figure 10a, b represents the 3D image of worn surfaces lubricated with pure and 0.05 wt% doped SiO_2 grease. It is clear from the 3D images that the furrows and grooves on the worn surfaces are more profound and sharp peaks are observed when tested against pure grease. Figure 10c shows a line profile of the worn surfaces of both the grease, and measured in the transverse direction of sliding. The line profile indicates that the roughness of SiO_2-doped grease was superior to the pure grease and their roughness values are summarized in Table 3.

The 3D image of the worn surface lubricated by SiO_2 doped grease exhibited lesser furrow marks and smooth surface as compared to the pure paraffin grease. Sometimes nanoparticles assist for abrasion of the mating surfaces and help in improving the surface roughness, called polishing effect (Lee et al. 2009). In the present study, SiO_2 nanoparticles demonstrated a polishing effect on the worn surface and it is visible in SEM (Fig. 8d) and it is also affirmed by AFM results. AFM analyses show that the average roughness (Rq = ~ 0.0307 µm) of the worn surface lubricated by SiO_2 doped grease is much lower than the average roughness (Rq = ~ 0.339 µm) on the worn surface lubricated with pure grease. This indicates that a remarkable improvement in the average roughness of the worn surface lubricated with SiO_2-doped grease. It is observed that doping of nanoparticles in grease enhanced lubrication behavior significantly by the surface modification.

The EDS analysis has been done for elemental characterization of the worn surfaces. Figure 11a, b represents EDS spectrum intensity peaks of worn surfaces lubricated with pure and 0.05 wt% SiO_2-doped paraffin grease, respectively. Figure 11a shows an intense peak of iron and some other elements of steel balls along with its atomic% and weight%. This has affirmed the absence of foreign particles in the pure paraffin grease. Figure 11b shows traces of the Si peak along with iron and some other elements of the steel ball. This Si peak is ascribed by the addition of the small fraction (0.05 wt%) into the paraffin grease. The presence of a Si element (0.23 wt%) shows its existence on the worn steel ball surface. This is an evidence for the presence of Si on the worn surface and forms a protective layer for separating the contacting surfaces (Ge et al. 2015).

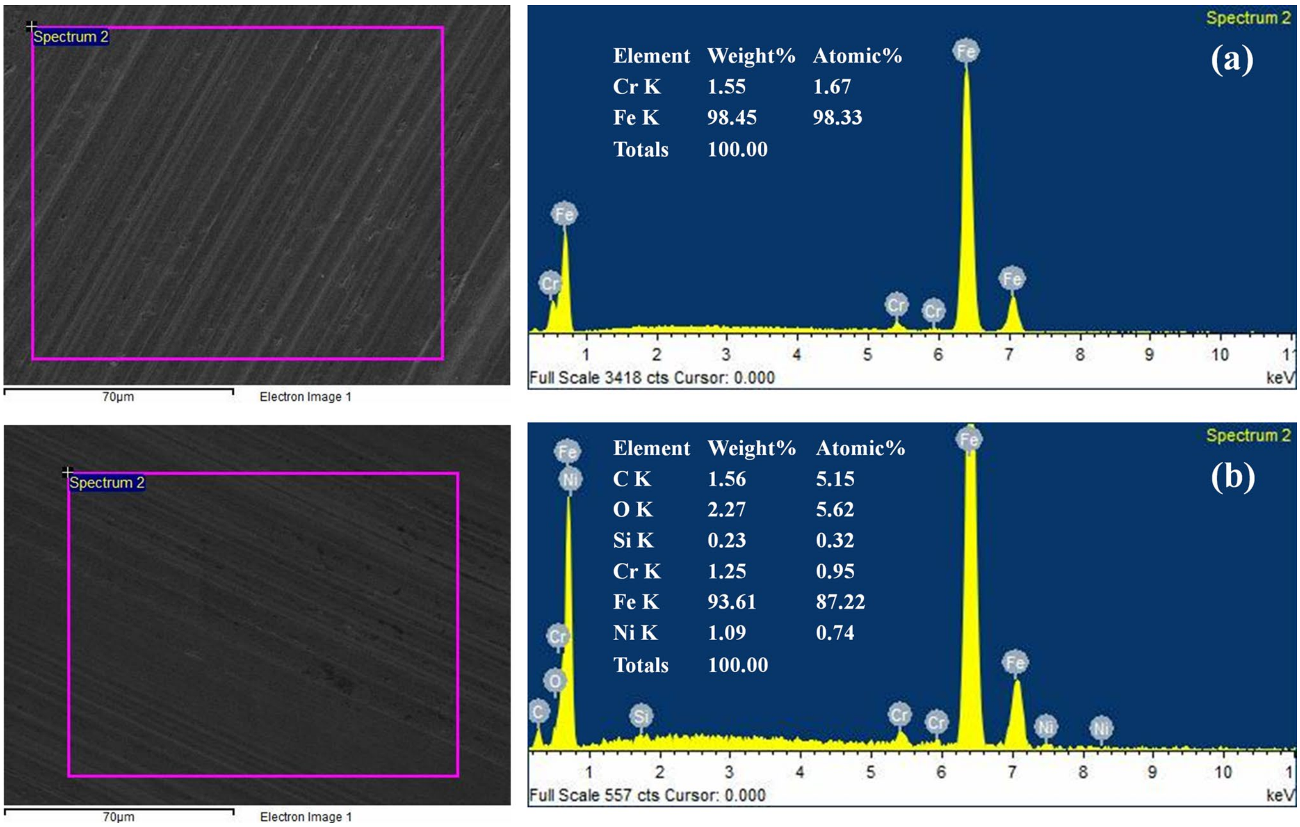

Fig. 11 EDS analysis of worn surfaces of steel balls lubricated with: **a** pure paraffin grease, **b** 0.05% w/w SiO_2 dispersed in paraffin grease

Summary of the work

The SiO_2 nanoparticles have been synthesized successfully with the modified sol–gel method. The various characterization techniques affirmed the formulation of SiO_2 nanoparticles. The shape of SiO_2 nanoparticles was almost spherical, and its average diameter was found to be ~70 nm. The grease was formulated with paraffin as a base oil and 12-lithium hydroxy stearate used as a thickening agent. The synthesized SiO_2 nanoparticles were used as an additive in the paraffin grease. The SiO_2 nanoparticles were dispersed in the paraffin grease by the in-situ method. The following conclusions have been drawn from the present study.

- The addition of SiO_2 nanoparticles in paraffin grease does not show any significant change in the physical properties, i.e., consistency, dropping point, water washout, leakage tendency, and evaporation loss.
- From the antiwear test, it has been observed that about ~20% reduction in the coefficient of friction at 0.03% w/w of nanoparticles, while ~42% reduction in the wear volume with the addition of 0.05% w/w of nanoparticles. The SiO_2 nanoparticles demonstrated as a polishing agent between the mating surfaces and help in improving the surface roughness properties.
- The addition of SiO_2 nanoparticles in the paraffin grease does not show any change in extreme pressure property. The last non-seizure and weld loads for both pure and SiO_2-doped paraffin grease were 126 and 160 kgf, respectively.
- The EDS spectrum showed the traces of Si on the worn surfaces, which confirms the protection of the surfaces against wear.

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