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Research Article

Preparation and evaluation of lubricating greases based on carbon nanotube

Refaat A. El-Adly[1] , Modather F. Hussein[2] and Alaa Mohamed[3]

[1]Egyptian Petroleum Research Institute, Nasr city, Cairo, Egypt

[2]Faculty of Science, Al-Azher University, Assuit Branch

[3]Faculty of Engineering, Cairo University.

email: Modatherepri82@gmail.com

ABSTRACT

The paper aims to preparing nano grease based on Multiwall carbon nanotube (MWCNTs) as additives. In this respect, the rheological and tribological properties of prepared nano greases with different of carbon nanotube content were studied. The microstructure of prepared carbon nanotube and nanao-greases were examined by high resolution transmission electron microscope (HR-TEM). The rheological properties of these greases with and without carbon nanotube-particles were explored at different temperatures using a brokfield rheometer. The experimental results reveal that improvement in the thermal and mechanical stabilities in addition to improvement in the oil separation. Also, the apparent viscosity increases with the increase of carbon nanotube concentration. The rheological characteristics of the obtained greases fitted with Herschel-Bulkley mathematical model. Tribological properties of the prepared greases with and without carbon nano-tube were evaluated using Pin-on-Disc tribometer. It was concluded that the prepared nano-greases have been proved to have quite favorable lubricating performance by the tribology experiments compared with blank grease.

Keywords: Nano grease, Carbon nanotube, Tribology and Rheology.

1. INTRODUCTION

Recently intensive efforts have been dedicated to the search for upgrading and evaluation of lubricating greases and their additives, a new frontier remains for researchers in the field of lubricating greases[1]. Lithium greases have good multi-purpose properties, e.g. high dropping point, good water resistance and good shear stability[2]. The preparation, evaluation and development of lithium lubricating greases from low cost starting materials such as, bone fat, cottonseed soapstock and jojoba meal were explored. Lubricating greases obtain their own properties from chemical additives, which are added to them [3-7].

In tribology, some nano materials have been proved to have great potential as lubricating materials or for development of advanced lubrication technology. So far, a number of nanocrystals have been synthesized and used as additives of lubricating oil [10–13]. They can greatly improve the antiwear capability, reduce friction coefficient, exhibit extreme pressure properties and even retard thermoinduced oxidation of lubrication oil/grease.

Nanotechnology is regarded as the most revolutionary technology of the 21st century. It can be used in many fields and ushers material science into a new era. There have been many investigations on the tribological properties of lubricants with different nanoparticles added. A large number of papers have reported that the addition of nanoparticles to lubricant was effective in reducing wear and friction [14–19].

Carbon nanotubes are one such nanomaterial whose existence was observed in 1990s. Due to superior physical and mechanical properties, carbon nano tubes have found its place in many critical applications. Due to its tubular structures and higher mechanical properties it can be predicted that carbon

nano tubes may work as rolling bearings without getting broken between two mating parts which may reduce the frictional coefficient and increase the load bearing capacity of the CNT based lubricant[8-9].
Hong et al. [20] investigated that CNT greases distinguish themselves from more common graphitic materials as solid grease additives. The performance of CNT grease could be much better with the improvement of nanotube quality and purity. Wang et al.[21] explored that when CaF_2 nanocrystals are used as lubricant additive in lithium grease, it improves the wear resistance, load carrying capacity and anti friction with the optimum concentration 1 wt%. Xianbing et al. [22] concluded that when $CaCo_3$ nanoparticles as an additive in lithium grease significantly improve its anti-wear performance, friction reduction property, load carrying capacity, and extreme pressure property with 0.5wt% optimum concentration. The purpose of the present study is to prepare carbon nano-tube by arc discharge and evaluate it as modifier for prepared lithium greases with different concentrations. With this aim, the physicochemical and tribological properties of prepared greases with and without carbon nano-tube were evaluated.
In addition, the performance of MWCNTs as an additive in lithium grease and the lubricating mechanisms have been discussed.

2. EXPERMENTAL

2.1. Materials

Graphite rode with purity 99.9 % , Mineral base oil was obtained from Al-Ameria Petroleum Company. Also 12-hydroxy-stearic acid, hydrogenated castor oil and lithium hydroxide were commercially obtained. All the experimental materials were used without further purification. The physicochemical properties of the base mineral oil which used as fluid for grease preparation was described elsewhere [17].

2.2. Synthesis of Multiwall carbon nano-tube

The multiwall Carbon nanotube (MWCNTS) under study was synthesized by the electric arc discharge apparatus as presented schematically in Figure 1. The full method disscused and described elsewhere [23]. In this method, the arc is generated between two electrodes (size φ 6 ×100 mm) using distilled water. The cathode and the anode are made from graphite (99.9% pure) and were performed under AC current, 75A and 238V.

2.3. Synthesis of prepared greases

The lithium grease designated (G1)was prepared as follows. First, mixture from 12-hydroxy stearic acid, hydrogenated castor oil, cotton seed soap stock and mineral base oil were added to a autoclave and the mixture stirred and heated to 120^{o}C until it became homogenous. Then oil slurry of lithium hydroxide monohydrate initially heated to about 110^{o}C was slowly added into the above mixture, then heated to 180^{o}C and held at this temperature for about 2-3 hours until complete saponification and thickening agent formed. Secondly, the remained base mineral oil added to lithium soap formed at temperature less than 80^{o}C to reach required consistency NLGI-2, then cooled to room temperature and milling to form the desired grease texture. The physicochemical and mechanical properties of the prepared grease was tested and classified according to the standards methods, National Lubricating Greases Institute (NLGI) and the Egyptian Standards (ES).
To investigate the effect of the carbon nano-tube on the properties and performance of prepared lithium grease. Three grades from nano- greases designated G2, G3 and G4 were prepared based on G1 with 0.1, 0.3 and 0.5 wt% of MWCNTs additive, respectively. One of the most effective factors on properties of nano-grease is the rate of dispersion and stability of nanoparticles in the lubricating greases. So, MWCNTs additives were added and mixing in second step in grease preparation with remained base mineral oil using ultra-sonication for 4 hr to ensure good dispersibility and prevent agglomeration.

2.4. Characterization

The physicochemical and mechanical properties of the prepared greases with and without MWCNTs were tested and classified according to the standards methods, National Lubricating Greases Institute (NLGI) and the Egyptian Standards (ES). The morphology, average size of CNTs and prepared nano-greases were examined using Transmission Electron Microscope JEOL 2010F- type-high contrast (HC). The microscope had accelerating voltage 200 kV. The samples for the TEM analysis were prepared by dropping a small amount of petroleum ether solution containing the CNTs or nano-grease onto 300 mesh copper grid and drying at room temperature.
The tribological behaviors of prepared nano grease with different concentration of MWCNTs were studied on a pin-on-disc machine equipped with a horizontal rotating disc and a dead-weight-loaded pin. The pin-on-disc machine was operated in a sealed box to ensure the cleanliness of the incoming air. Before testing, the disc specimens were cleaned for 20 minutes with acetone. Friction tests for prepared nano greases were conducted on pin on disc tribometer at a rotating speed 150, 250 and 400 rpm and load 50 N, under 15 min test duration

The rheological behaviour of the prepared greases was carried out at temperature 90^{o}C. At least two or triplicates of each test were performed on fresh samples. This behaviour was carried using Brookfield programmable Rheometer HA-DV-III UITRA used in conjunction with Brookfield software, RHEOCALC V.2. Through RHEOCALC, all Rheometer functions (rotational speed, instrument % torque scale, time interval, set temperature) are controlled by a computer.

3. RESULT AND DISSCUSION

Lubricating greases are semisolid or solid colloidal dispersions owing their consistency to a gel-type network. The development of lubricating grease with the right consistency requires stringent optimization of components and preparation scheme. The function of grease is to remain in contact with lubricate moving surfaces without gravity or centrifugal action, or be squeezed out under pressure.

3.1. Microscopic behavior of carbon nanotube

The higher resolution of the electron microscope is necessary to examine the thickener and additive morphology that contribute so much to the performance of lubricating greases.

Figure 1 shows the transmission electron microscope (TEM) images of MWCNTs. The tubular and filamentous morphology of nanotubes are shown very clear in the presented image. This image shows the prepared MWCNTs have an average diameter ranging from 5 to10nm.

3.2. Physico-chemical properties of prepared grease without CNTs

To evaluate effect of mineral oil and fatty materials, the prepared grease G1 has been formulated according to ingredients listed in Table1. It was shown that remarkable improvement in mechanical and thermal properties as indicated in penetration value 285 and dropping point 195^{o}C, respectively .This reveal that the fatty materials mixture having synergistic effect during saponification reaction. So, it could be speculate that, one of the soap predominates and determines the properties of the grease while the other modifies the grease texture and improves mechanical stability.

Figure 2 shows that the transmission electron microscopy (TEM) of lithium soap of G1 on a carbon film substrate. It shows that the Lithium soap has fibers or soap aggregates with width or diameter of 0.5 micron or less leads to more interlocking with base mineral oil. This reveal that the obtained grease developed with chain length of the mixture of fatty acids (cotton soap stockm, hydrogenated Castor oil and 12 hydroxy stearic acid).

3.3 Physico-chemical properties of prepared grease with multiwall carbon nanotube

Table 2 shows the physico-chemical properties of the prepared greases G2, G3 and G4 with different concentrations of MWCNTs 0.1, 0.3 and 0.5 %, respectively. The obtained data in this table reveal that significantly improvement in the dropping point, penetration and apparent viscosity.

Figure 3 shows the TEM of MWCNTs dispersed in lithium soap .It can be seen that there is no apparent aggregation of MWCNTs, indicating that the MWCNTs could be well dispersed in lithium grease which indicates the good distribution of the MWCNTs with prepared greases. Hence, proper sonication has to be done in order to overcome the agglomeration of the MWCNTs. Due to enormous aspect ratio and small diameter of MWCNTs, a strong Vander-Waals attraction exists between the MWCNTs which results in bundling of MWCNTs. In addition to observed that the microscopic structure of lithium grease presents amore regular and homogeneous network structure which confirm the improvement of thermal mechanical and rheological behavior.

3.4 Tribological performance of prepared greases

The coefficient of friction plays a major role in determining the transmission efficiency via moving components where less resistance contributes to higher efficiency. Therefore, in terms of lubrication, less frictional coefficient is desirable.

Figures 4-6 show the effect of the friction coefficients of nano greases G2, G3and G4 by addition different concentration of carbon naotube (0.1, 0.3 and 0.5%) under severe sliding conditions 150, 250 and 400 RPM.

Figure 4 show the friction coefficients of nano greases at different time at150 RPM. It observed that the friction coefficients decrease significantly by the concentration of MWCNTs by 8.9, 20.3 and 42.6% for 0.1, 0.3 and 0.5% respectively.

Also in fig 5, under sliding 250 RPM, the friction coefficient decreased by 11.9, 24.5 and 37.1% by addition the above-mentioned concentration of CNTs respectively

Under sliding 400 RPM, the friction coefficient decreased by 11.7, 23.5 and 35.2% respectively by addition the above-mentioned concentration of CNTs as fig 6.

A summary of what has been described above in the previous three figures that the friction coefficients decrease with increasing of CNTs concentration.

These results indicate that the friction-reduction ability of prepared grease become far well by adding the above concentrations of CNTs. This indicate that the frictional reduction property and the antiwear property depend on the concentration of the MWNTs.

3.5. Rheological peoperties of nano greases

The apparent viscosity of grease is an important basic characteristic. It is a key parameter of computational fluid lubrication and has a significant impact on machine performance. Thus, the analysis of apparent viscosity of grease containing MWCNTs provides an important reference to select the right grease for equipment with adequate lubrication.

Fig.7&8 show the influence of the MWCNTs-particle concentration on the apparent viscosity of prepared nano greases. As can be seen, the apparent viscosity increases with increase of the nano-particles content within the ratio of MWCNTs added.

Fig 7 shows plastic flow behavior with yield stress for the prepared greases.

The mathematical analysis of the flow behavior curve(shear stress- shear rate) for the prepared greases are fitted with Herschel-Bulkley model.

As presented in Fig. 8, the prepared greases have clear shear-thinning properties. The shear-thinning phenomenon of the prepared greases G2, G3 and G4 containing MWCNTs are more evident than G1. The shear-thinning properties of grease have a special adaptation on machinery whose speed frequently changes. When the speed is high, low viscosity lubricant is required. When the speed is low, high viscosity lubricant is required. Therefore, the shear-thinning properties of grease are in line with the mechanical speed change on the request of lubricant viscosity [25].

3.6. Mechanical stability of prepared greases

The effect of mechanical work at different double strokes from 0 to 10000 strokes on penetration for the prepared nano greases based on CNTs (G1, G2 G3 and G4) illustrated in figure 9.

This figure reveals that the high concentration 0.5% CNTs have a large influence on the mechanical stability of G4 compare with G3 and G2. Also, G4 more resist to deformation in consistency compare G3 and G2.

3.7. Thermal stability of prepared nano greases.

The structural changes in lubricating greases due to temperature are mainly due to phase changes in the thickening agent. As the temperature of lubricating greases is raised, the thickener softens stepwise due to phase transitions. At lower transition temperatures, such softening may be great enough to permit the nano grease to flow. The dropping point, therefore, is reached below the true melting point of the thickener. As the thickener fibers soften, they may also swell; this swelling depends upon the fluid.

Experimental data graphically presented in Figure 10, show the variation of the dropping point with the mechanical work at different double strokes from 0 to 10000 as a function of binding forces between ingredients and degree of compatibility of thickener with lithium soap.

It shows that with the increase of the mechanical work, the dropping points decrease in the following order: G4> G3> G2>G1,. This explanation consistent with the data concerning apparent viscosity and penetration for greases under investigation.

4. CONCLUSION.

According to the experimental results the following can be concluded:

1) The arc discharge apparatus is a good method to produce MWCNTS

2) The apparent viscosity increases with the increase of MWCNTs concentration.

3) The grease with and without the nano-particles both have yield stresses and clear shear-thinning properties. The shear-thinning phenomenon of the grease containing CNTs particles is more evident than that of the basic grease. The experimental results also reveal that the rheological characteristics of both types of grease fitted with in Herschel-Bulkley model.

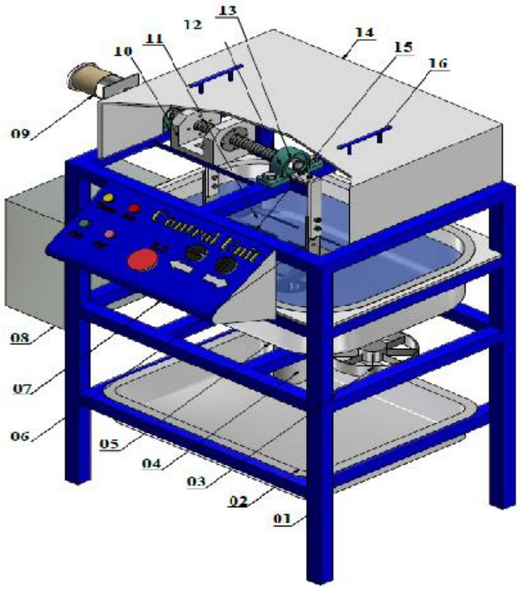
4) Nano-particles have a significant influence on the rheological parameters. The yield stress and the flow index of the grease containing nano-particles are smaller than that of the basic grease, but the plastic viscosity is larger.

Table 1
Effect of the fatty material on characterization of the ingredient greases

Ingredient	G_1	Test method
Base oil, Wt %	85	
Cotton seed Soap stock, Wt %	1	
Hydrogenated castor oil, Wt %	2	
12- hydroxyl stearic acid, Wt %	12	
Penetration		
Un worked	285	ASTM D-217
worked	300	
Dropping point, °C	195	ASTM D-566
Copper Corrosion 3h/100°C	Ia	ASTM D-4048
Oxidation Stability 99± 96h, pressure drop, psi	12	ASTM D-942
TAN, mg KOH/gm @ 72h	0.70	ASTM D-664
Oil Separation, Wt%	2.2	ASTM D-1724
Code grease according to NLGI	2	
Egyptian standard	LB	
Apparent Viscosity, cP, @ 90 °C	29430	ASTM D-189
Yield stress, D/cm^2	73.2	

Table 2
Effect of the concentration of MWCNTs on characterization of the prepared greases

Ingredient	G_2	G_3	G_4	Test method
MWCNTs additive, Wt %	0.1	0.3	0.5	
Penetration				
Un worked	274	271	265	ASTM D-217
Worked	280	276	270	
Dropping point, °C	196	200	220	ASTM D-566
Copper Corrosion 3h/100°C	Ia	Ia	Ia	ASTM D-4048
Oxidation Stability 99± 96h, pressure drop, psi	8	6	5	ASTM D-942
TAN, mg KOH/gm @ 72h	0.63	0.61	0.50	ASTM D-664
Oil Separation, Wt%	2.0	1.9	1.9	ASTM D-1724
Code grease according to NLGI	2	2	2	
Egyptian standard	LB	LB	LB	
Apparent Viscosity, cP, @ 90 °C	32060	33408	36032	ASTM D-189
Yield stress, D/cm^2	85.5	89	101.3	



Part No.	Description
01	Base Frame
02	Lower Tank
03	Fans for Cooling
04	Valve
05	Upper Tank
06	Carbon Holder
07	Control Unit
08	Electrical Unite
09	Steeper Motor
10	Nuts Housing
11	Deionized water
12	Power Screw
13	Bearing
14	Cover
15	Pure Graphite
16	Cover Hand

Scheme 1
Schematic illustration of arc discharge

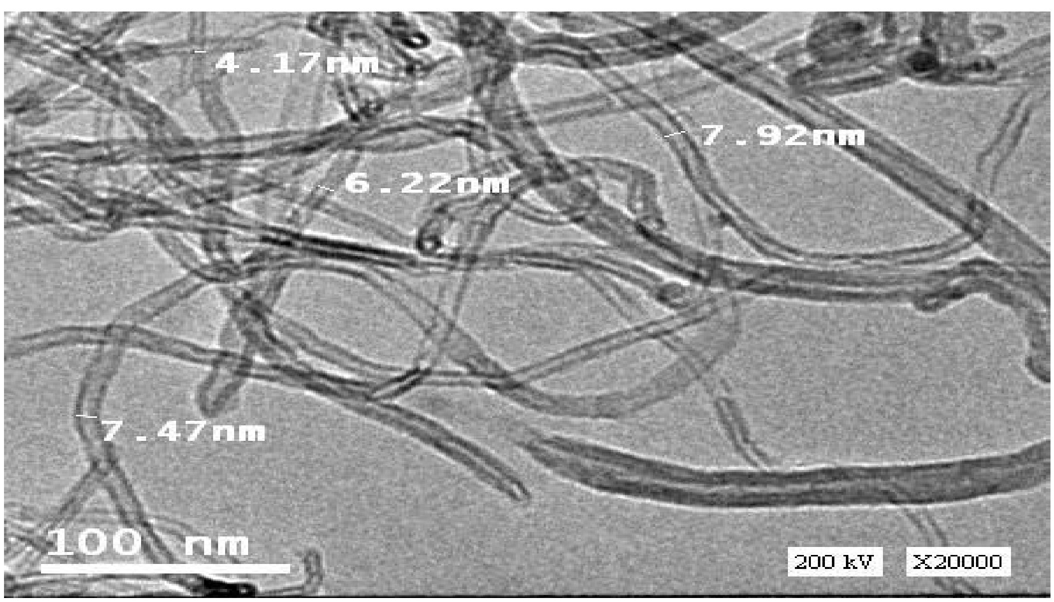


Figure 1
TEM image of multiwall Carbon nanotube

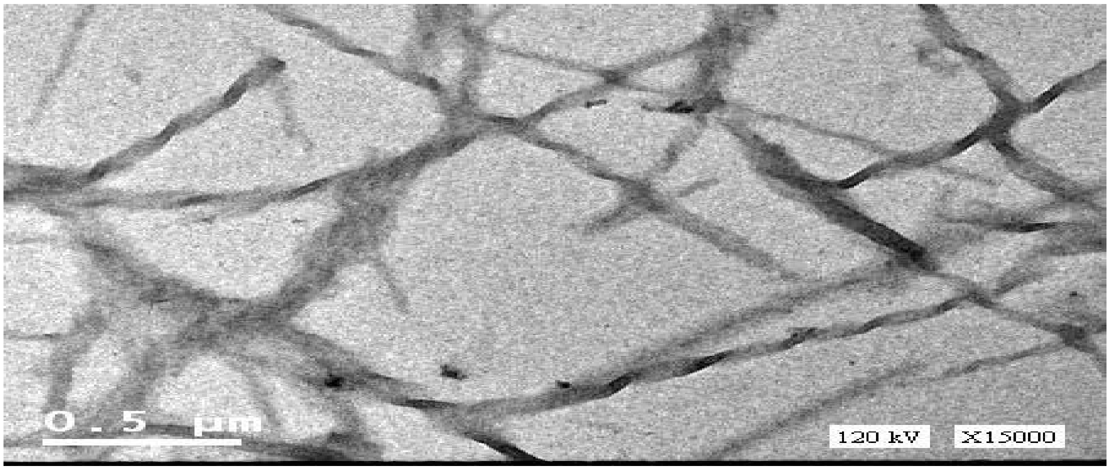


Fig 2
TEM image of prepared grease fibrous

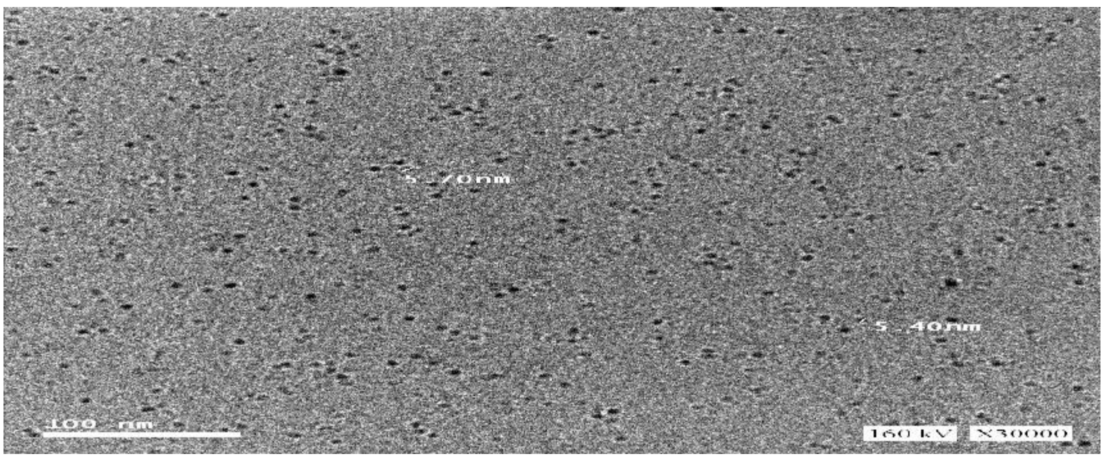


Fig 3
TEM image of Carbon nanotube dispersed in lithium soap G4

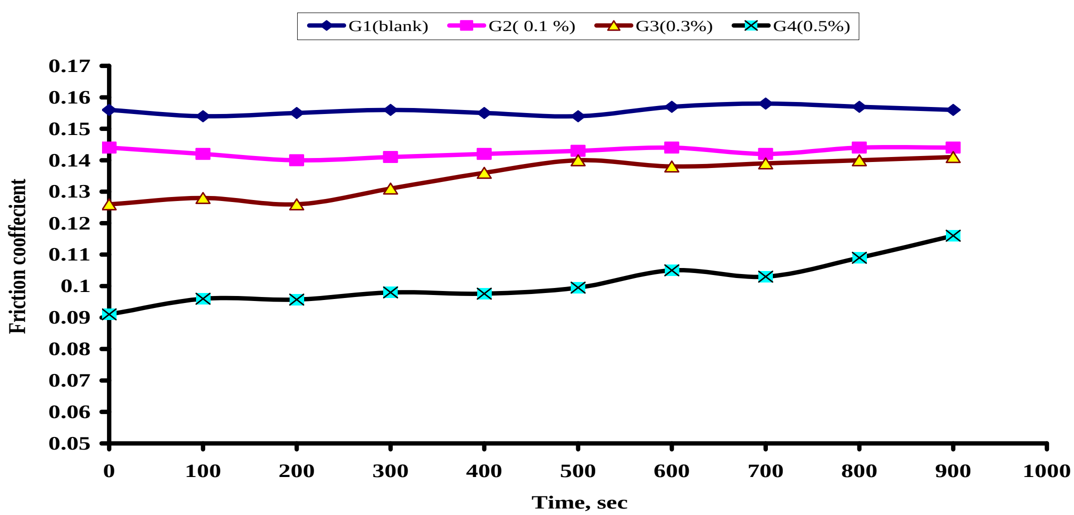


Fig 4
Tribological properties of nano greases at 150 RPM

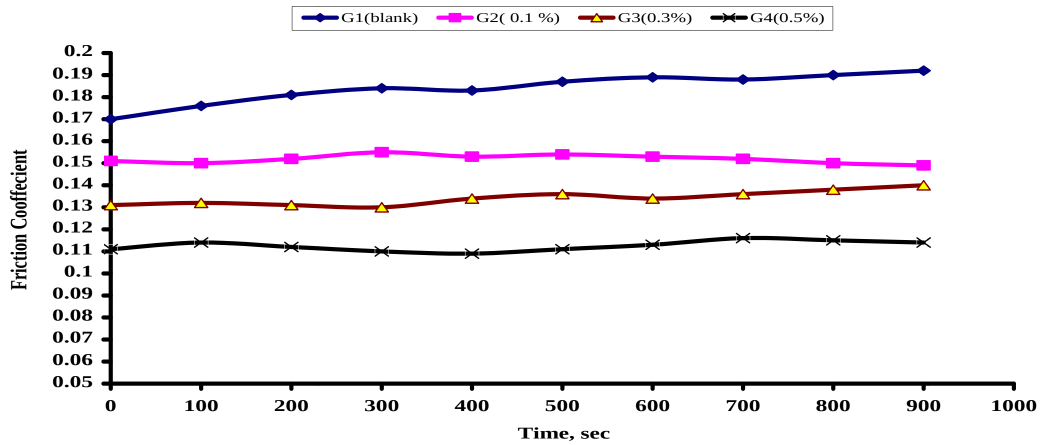


Fig 5
Tribological properties of nano greases at 250 RPM

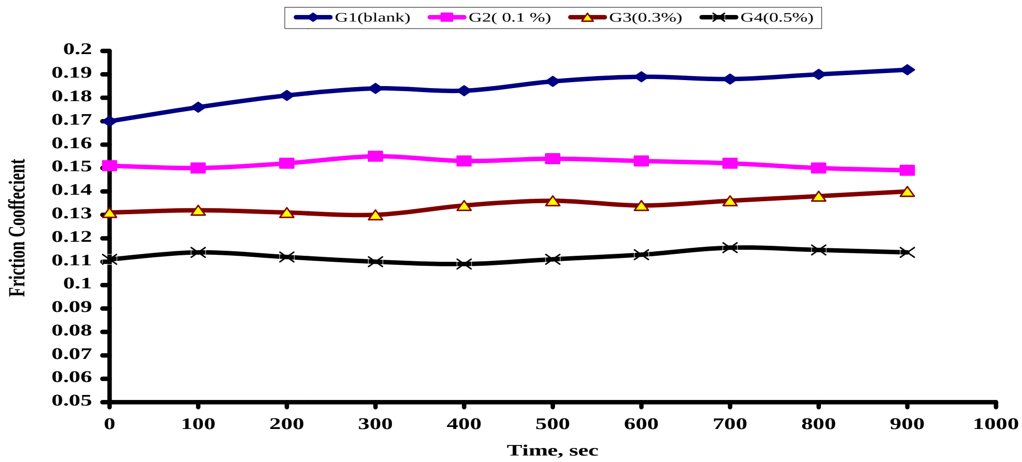


Fig6
Tribological properties of nano greases at 400 RPM

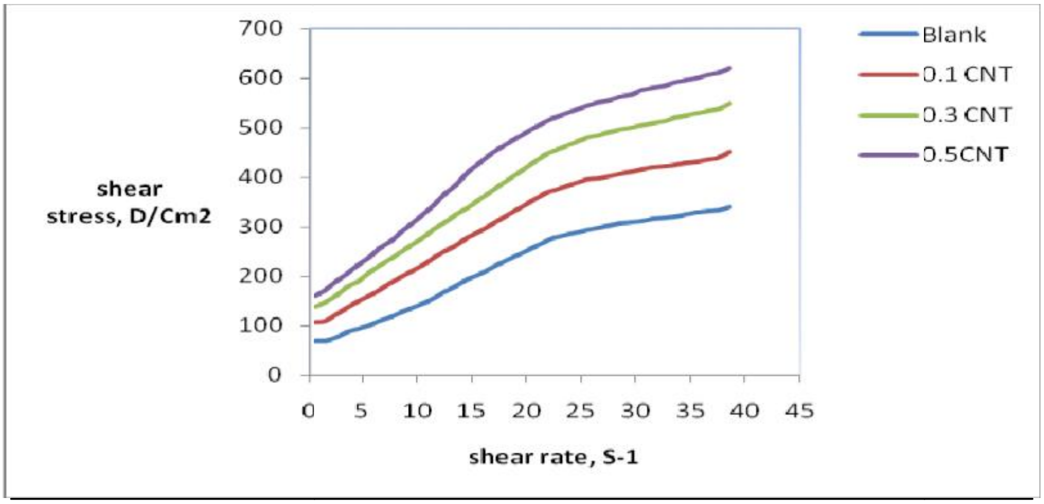


Fig 7
variation of shear stress- shear rate of prepared nanogreases@90^{o}C

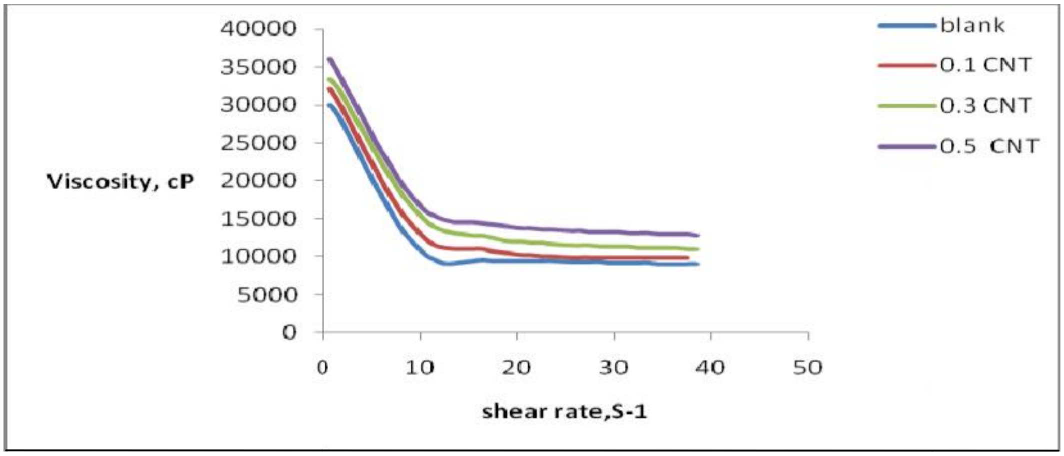


Fig 8
variation of viscosity - shear rate of prepared nanogreases@90°C

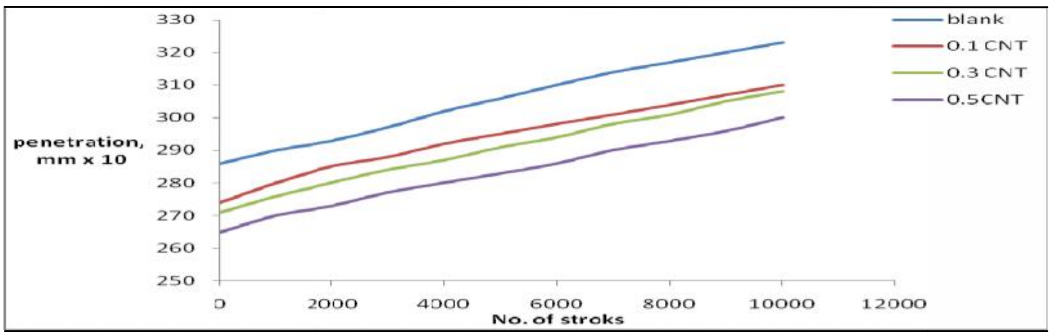


Fig 9
Mechanical stability of prepared greases

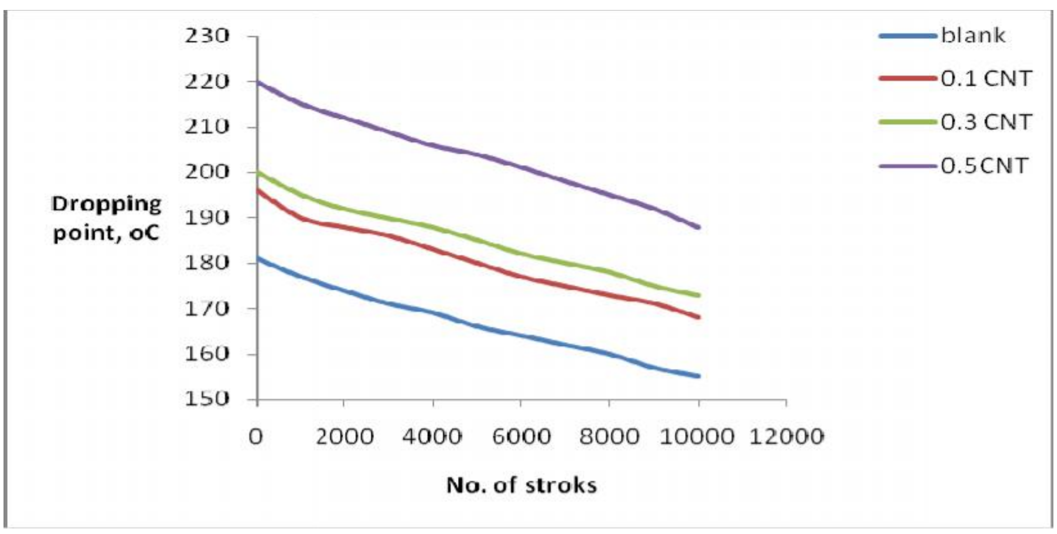


Fig 10
Thermal stability of prepared nano greases

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