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Impact of tribo-morphological transformation of graphene on the viscosity of engine oils

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ABSTRACT – One of the major factors that determines the choice of engine oil is its viscosity. This research investigates the impact of graphene on the viscosity of engine oil before and after IC engine operation. Morphological changes of the graphene flakes have been studied to understand its dependency on the rheological performance of engine oil. Graphene based nanolubricants were synthesized to meet API SN/CF 20W50 grade. Scanning electron microscopy graphs show that the graphene flakes undergo tribo-morphological transformations to become tubes, helical coils and percolated structures. However, such changes do not significantly impact the viscosity of engine oil throughout its life-cycle.

1. INTRODUCTION

Fast advancing automotive industries continue their pursuit of improving heat transfer from engines for better performance. Commonly used lubricants have inherently poor thermal conductivities that limit the heat transfer significantly. To overcome this drawback, a number of chemical based additives are blended with base oils. Nanoparticles which are being introduced as lubricant additives have an edge over the traditional thermal additives owing to their remarkable thermo-physical properties. Nanoparticles not only improve lubricant thermal conductivity but also significantly alter its viscosity [1]. Many engine oil formulations already contain viscosity modifies such as olefin copolymer (OCP) and polymethacrylate (PMAs). Original equipment manufacturers (OEMs) favor the lubricants to be within certain viscosity range. If the addition of nanoparticles to formulations alters its viscosity, it will limit its potential to be an additive. Moreover, if variations in lubricant viscosity are observed during engine operation, it might further restrict the use of nanoparticles as additives. Oils containing nanoparticles, popularly known as nanolubricants or nanofluids witness change in viscosity of base oils with the increasing nanoparticle concentration and temperature. Few reports have also found a relationship between thermal conductivity and viscosity of nanofluids [2, 3]. Discrepancies exist over the relationship between viscosity and various other physical parameters [4]. However, recently discovered graphene has the advantage of causing negligible changes to lubricant viscosity [5]. Graphene is one layer of atomic carbon with theoretical specific surface area up to 2600 m^2g^{-1} [6] and excellent in-plane thermal conductivity up to 5200 $Wm^{-1}K^{-1}$ [7]. Compared to graphene based oils, polar solvents such as water and ethylene glycol based nanofluids have been investigated more. Viscosity enhancements ranging between 15-100% has been witnessed for several polar solvents. Very little or no explanation has been provided to justify the observed behavior of graphene based suspensions. In this study, kinematic viscosity and dynamic viscosity of graphene nanolubricant before and after subjecting to engine test has been investigated. Factors such as the graphene size, temperature and lubricity additive concentration have been considered.

2. METHODOLOGY

Engine oil meeting API 20W50 SN/CF specifications and natural polymeric ester based lubricity additive are obtained from Lube World, Sdn Bhd, Malaysia and Apar Industries Limited, India. Graphene nanopowders have flake thickness approximately 8-12 nm were procured from Graphene Labs Inc, USA. Sample of nanolubricants are prepared by blending different ratios of graphene, oil and the additive. Stirring and 4 hours of sonication was performed using bath type sonicator (JAC Sonicator 1505, 4 kHz) to obtain homogeneous formulation. The samples were physically monitored to examine settling of nanoflakes. Morphology and elemental composition of graphene was characterized using Field Emission Scanning Electron Microscope (FESEM FEI Quanta 400F, USA). XRD pattern was acquired by producing X-rays with a voltage of 45 kV and 27 mA through copper material, with wavelength (K alpha) of 1.54 Å and filtration of x-ray through Ni using PANytical X-ray Diffractometer, Netherlands. Kinematic Viscosity at 40 and 100 ºC was measured using ASTM D 445 standard procedure. Dynamic viscosity was measured using Anton Paar rheometer MCR 302. The used engine oils were obtained from our previous study [8], where the methodology of engine tests and used oil analysis is described in detail.

3. RESULTS

The engine oil properties were determined using the ASTM standards mentioned in the Table 1.

Table 1. Engine oil properties

Property/characteristics	Test Method	API SN/CF 20W50
Appearance	Visual	Clear Liquid
Colour visual	ASTM D 1500	< 2.0
Density at 29.5 C, gm/cc	ASTM D 1298	0.865
Viscosity at 40^{o}C, kinematic, cSt (mm^2/s)	ASTM D 445	159.7
Viscosity at 100^{o}C, kinematic, cSt (mm^2/s)	ASTM D 445	18.45
Viscosity index	ASTM D 2270	130
TAN, mgKOH/gm	ASTM D 974	1.22
TBN, mgKOH/gm	ASTM D 2896	8.12

The morphology of graphene analysed using SEM (Figure 1) shows that the structure of graphene in powder for is predominantly planar. The corresponding EDX graph shows the pristine nature of graphene.

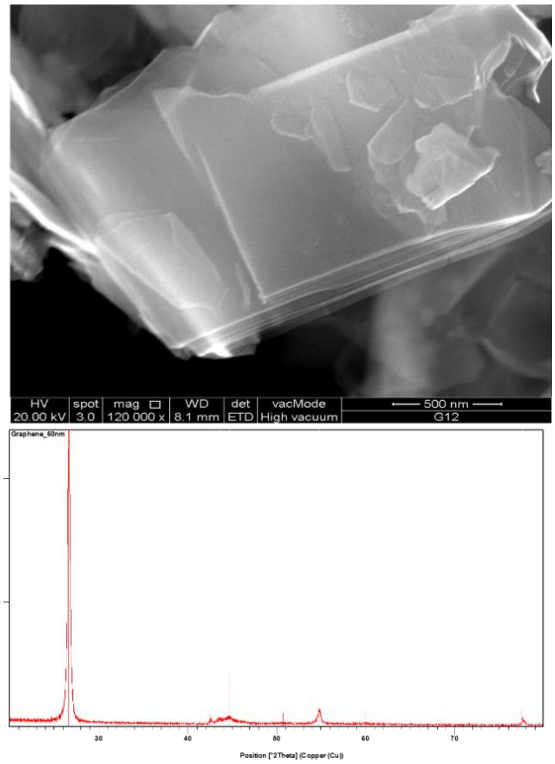

Figure 1. SEM images of graphene flakes used in the study. E: EDX corresponding to figure A.

The dynamic viscosity results of the virgin oil and graphene nanolubricant confirmed its Newtonian behaviour. The kinematic viscosity of the oil without and with graphene had insignificant difference (157.20 mm^2/s) after the engine operation for 100 hrs. Graphene in the oil was found to undergo substantial morphological transformation (Figure 2) owing to several tribological phenomenon however, that did not affect oil viscosity.

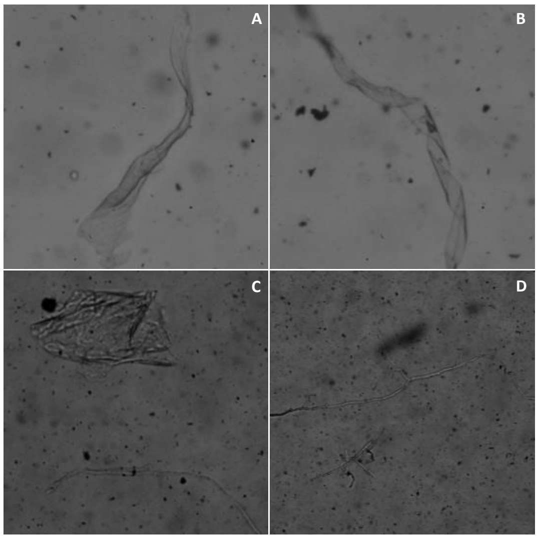

Figure 2. Graphene in oil before engine test, A - partially rolled, B – Twisted; Graphene in oil after engine test, C - Fulled rolled and partially exfoliated, D – Percolated and Entangled;

4. CONCLUSION

Graphene added to improve the anti-wear and thermal properties of the oil undergoes several tribo-morphological transformations. However, that does not affect the viscosity of oil before and after 100 hrs of engine operation.

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