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# Study of graphene nanolubricant using thermogravimetric analysis

A.K. Rasheed[1], M. Khalid[1,*], W. Rashmi[2], T.C.S.M. Gupta[3], A. Chan[4]

[1)] Manufacturing & Industrial Processes Division, Faculty of Engineering, University of Nottingham, Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor, Malaysia.
[2)] Energy Research Division, Taylor's University, Lakeside Campus, 47500 Subang Jaya, Selangor, Malaysia.
[3)] Lube World Holdings Sdn Bhd, Petaling Jaya, Malaysia.
[4)] Environmental Research Division, Faculty of Engineering, University of Nottingham, Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor, Malaysia.

[*]Corresponding e-mail: Khalid.Siddiqui@nottingham.edu.my

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**ABSTRACT** – Thermal degradation of graphene based mineral oil lubricants was studied using thermogravimetric analysis (TGA). As-synthesized graphene sheets of 8, 12, 60 nm thick, engine-oil formulation of API standard 20W50 SN/CF, SJ/CF and base mineral oils 150, 500, 2100 SUS were used for synthesizing various test samples. FTIR, XRD, FESEM, EDX, zeta potential and UV-vis spectrophotometry was used to characterize graphene and nanolubricants. Thermal gravimetric analysis (TGA) revealed that the weight loss in the presence of graphene could be delayed by more than 20 °C. Resistance to oil degradation depends strongly on graphene nanoparticle size, concentration and heating rates. Moreover, with the addition of graphene, SN/CF oil formulation shows better enhancement than SJ/CF under most parameters. The reasons for this phenomenon could be attributed to graphene's large surface area, stable dispersion and Brownian motion of graphene flakes.

## 1. INTRODUCTION

Improving lubricant properties has been an indispensable area of research for many decades. Several additives were introduced to enhance thermal and lubricating properties of the lubricants yet the efficiency is compromised. Recently it was shown that the addition of nanometer sized (1-100 nm) particles to liquids could significantly enhance various properties of base fluids. Such nanoparticle suspensions are widely known as nanofluids or nanolubricants [1]. CNT nanofluids were found superior to most of the metallic and oxide nanofluids in terms of enhanced thermal conductivity. Nonetheless, the discovery of graphene nano-flakes [2] made it possible to synthesize nanofluids with much better efficiency. Graphene nano-flakes are made of one layer of atomic carbon with theoretical specific surface area up to 2600 $m^2/g$. In addition, it has excellent in-plane thermal conductivity which can be as high as 5200 W/m-K [3]. Although a few oil based nanoparticle suspensions have been investigated [4, 5] for its thermal conductivity and viscosity, SAE standard engine oil formulation based graphene nanolubricants have not been thoroughly investigated. In this study, we have investigated the thermal degradation of graphene based API standard SN/CF and SJ/CF 20W50 engine oil formulations using TGA. The experimental results were also compared with TGA kinetic models.

## 2. MATERIALS AND METHODOLOGY

Graphene flakes (Table 1) were purchased from Graphene Labs Inc, USA. The graphene powder was suspended in mineral oil at 0.01 wt% concentration (Figure 1). To ensure proper mixing of the nanoparticles in oil, stirring and sonication was performed for 4 hours using bath-sonicator (JAC Sonicator 1505, 4 kHz). The samples were physically monitored to examine settling of nanoflakes. UV-Vis spectroscopy (Perkin-Elmer Lambda 35) was performed to confirm the characteristic peak of the samples.

Table 1 Graphene dimensions as per supplier.

| Material (thickness, nm) | Specific surface area | Lateral dimensions (nm) |
|---|---|---|
| Graphene (60) | <15 $m^2/g$ | 3000 - 7000 |
| Graphene (12) | 80 $m^2/g$ | 1500 - 10000 |
| Graphene (8) | -100 $m^2/g$ | 150 - 3000 |

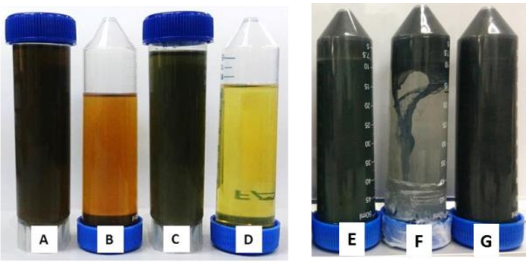


Figure 1 Engine oil samples (0.01wt%) representing stability. A – 20W50 SJ/CF+G60 nm; B-1:20 dilution of A; C – 20W50 SN/CF+G60 nm; D-1:20 dilution of C; E – 150 SUS; F – 500 SUS; G - 2100 SUS.

The graphene nanoflakes were mounted on stubs with conductive carbon tape and coated with platinum using JEOL JFC-1600 auto fine coater. All the samples were analyzed for their morphology and elemental compositions with energy-dispersive X-ray spectroscopy (EDX) using SEM (JOEL JSM 6400 LV, Japan). Thermal degradation studies were performed using Simultaneous Thermal Analyzer (STA) 6000, Perkin Elmer. Oil samples (<15 mg) were analyzed under nitrogen gas at a flow rate of 20 ml/min. The samples were maintained at 30°C isothermal state and then gradually raised up to 800°C with a heating rate of 5°C/min, 10°C/min, 15°C/min and 20 °C/min according to the desired experiment.

## 3. RESULTS

The characteristic spectra of graphene nanolubricant were observed for various concentrations. The absorbance was increasing with the increase in concentration and the peak was observed approximately at 225 nm wavelength.

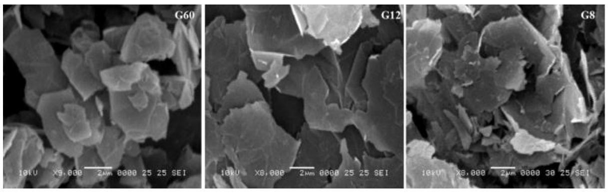

Figure 2. Scanning electron microscope graphs of graphene: 60, 12 and 8 nm thick.

The SEM images with 2 µm magnification shows the physical nature of graphene flakes in powder form, Figure 2. The as-synthesized graphene is hydrophobic in nature and it does not disperse well in polar solvents. After EDX analysis, using quantitative method the graphene flakes were analyzed and normalized results were obtained. The composition comprised of C - 92.89% and Zr – 7.11%. Although the dispersion was not observed under a microscope, it is expected that the sonication would enable the graphene flakes to disperse uniformly. Zeta potential results (not shown) indicate that that functionalized graphene in water and the as-synthesized graphene in the oil formulation is stable over a month. Particle agglomeration, hydrophobicity, fluid polarity, surface charges of the particle and other factors determine the stability of the suspensions. The pure base mineral oil as seen in the figure 1 has poor stability owing to particle agglomeration and strong nonpolar nature.

### *3.1 Thermogravimetry Results*

Figure 3 indicates that the addition of graphene could delay the oxidation by around 20 °C. Moreover, the weight loss during the oxidation could be delayed by over 20-40 °C. The size has considerable effect on the thermal conductivity, and as a result affects the weight loss. Figure 4 shows that similar thermal behavior could be observed in SJ/CF oils however, the enhancement is comparatively low when compared with SN/CF.

It is well known from the existing reports on nanofluids that the inherently stochastic motion of nanoparticles could be a probable explanation for the thermal conductivity enhancement since smaller particles show greater enhancements of thermal conductivity with temperature. Similarly, elevated temperature might modulate random motion of graphene nanoparticles in fluid and thus resulting in considerable enhancement of thermal properties.

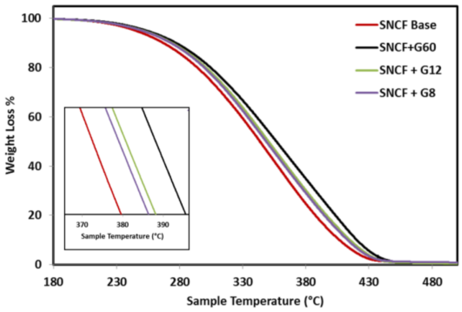

Figure 3 TGA plots with a heating rate of 5 °C/min under nitrogen.

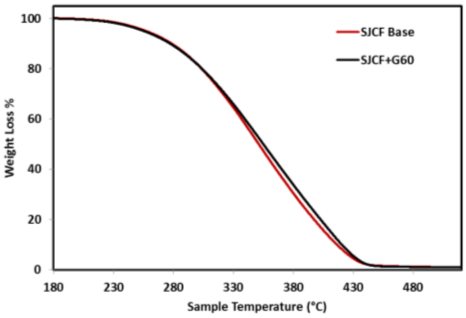

Figure 4 TGA plots of SJ/CF oil with a heating rate of 5 °C/min under nitrogen.

## 4. CONCLUSION

The addition of graphene to mineral oils can significantly enhance the thermal properties. The enhancement depends on graphene size, concentration and heating rates. Stability of the nanolubricant is vital to retain the enhanced thermal properties.

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