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ENHANCING DISPERSION STABILITY OF NANO-STRUCTURED TITANIUM OXIDE /GRAPHENE OXIDE IN MINERAL AND BIO-BASED ENGINE LUBRICANT FORMULATIONS

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ABSTRACT: New strategies are needed to reduce friction and wear in internal combustion (IC) engines. This will help save energy, extend the life of engine components, reduce the depletion of fossil fuel reserves, and decrease the production of waste crankcase oil, addressing current environmental issues. Nano-additives have shown promising results in improving the tribological performance of lubricants. However, the stability of nanoparticle dispersion in nano-lubricants remains a challenge for the effective use of nanomaterials as lubricant additives. This research investigates the efficacy of nanocomposite materials containing graphene oxide (GO) and reduced graphene oxide (r-GO) for reducing friction. Ultrasonication was used to create four different formulations: added graphene (G) and GO to the mineral-based engine oil (15W40), TiO_2/G, and TiO_2/r-GO with formulated coconut oil (FCO) as the base stock to blend sample lubricants. The dispersion stability of all four samples was tested using a UV-visible spectrophotometer, keeping 15W40 as the reference. Tribological performance was assessed using a linear reciprocating tribometer (LRT) test rig, which confirmed that lubricants containing GO and r-GO nano-additives exhibited improved lubricity. The sample containing 15W40 with GO as nano-additives and the sample with FCO containing TiO_2/r-GO as nano-additives showed a 26% and 23% reduction in Coefficient of Friction (COF) over 15W40, respectively. The addition of GO and r-GO improved the dispersion stability of sample lubricants, leading to an enhancement in tribological characteristics due to the oxygen-containing functional groups attached to nanocomposite structures.

Keywords: nano-additives, dispersion stability, oxygen functional groups, engine lubrication

1 INTRODUCTION

The ultrafine size of the nanoparticles, which allows them to infiltrate between the asperity contacts of surfaces in relative motion, is a promising solution for improving the efficiency of internal combustion engine (ICE) lubrication. This scale-dependent behaviour, along with their adhesion and cohesion properties, enables them to roll between sliding surfaces and also to create a boundary layer, which can enhance the lubricant characteristics during combustion (Ali et al., 2016). Nevertheless, many researchers have reported agglomeration and sedimentation of nanoparticles within mineral base oil over an extended period of storage time (Ali et al., 2016; Syahir et al., 2017).

This research explores methodologies to improve the dispersion stability of nano-additives in engine lubricants with specific focus on: a) comparing the stability of graphene (G) and graphene oxide (GO) in mineral-based multi-grade engine oil 15W40; b) the stability between titanium dioxide/graphene (TiO_2/G) and titanium dioxide/reduced graphene oxide (TiO_2/r-GO) in formulated coconut oil (FCO) as a bio-based lubricant.

There are many nano-additives associated with lubricant formulation that have shown improved tribological performance. For example, Ali et al. (2016) used TiO_2 nanoparticles in 5W30 mineral oil and reported a reduction of the Coefficient of Friction (COF) and the wear rate, compared to the reference oil (5W30). Meng et al. (Meng et al., 2016) reported the reduction of COF and WSD using mineral oil 10W40 as base-stock to blend with supercritical (Sc)-Ag/graphene nanocomposite as nano-additives.

The importance of achieving an optimum particle concentration to enhance the dispersion stability of nano-additives in base-stocks, thereby avoiding agglomeration and sedimentation, was noted by Singh et al., 2019), which leads to minimizing friction and wear in the nano-lubricant. In another development, it has been shown that the presence of sufficient oxygen groups makes graphene oxide/reduced graphene oxide (GO/r-GO) nanocomposites compatible with dispersion in polar liquid lubricants (Gupta et al., 2017). Gulzar et al. (2017) emphasised the importance of smaller particle size and method of agitation in enhancing colloidal stability.

2 EXPERIMENTAL METHODOLOGY

In this research, the dispersion stability of nano-additives was investigated in two different base fluids: 15W40 with graphene and graphene oxide, and formulated coconut oil (FCO) with the nanocomposites TiO_2/G and TiO_2/r-GO. TiO_2/G and TiO_2/r-GO nanomaterials were synthesized via thermal annealing and continuous hydrothermal flow synthesis (CHFS) routes, respectively, and characterized, including graphene for confirmation.

2.1 Material

Mineral-based 15W40 is widely used globally in heavy-duty engines and was therefore chosen as the reference oil for comparison results, in addition to serving as the mineral base stock. FCO is a locally available vegetable oil used as a bio-based lubricant stock to reduce reliance on petroleum-based lubricants and promote environmental sustainability. Graphene, graphene oxide, precursor titanium bis-ammonium lactato dihydroxide (TiBALD; Ti^{+4}), KOH, and other chemicals were used in this research.

2.2 Synthesis and characterization of nano additives of interest

The CHFS method was used to synthesize nano-additives TiO_2 and TiO_2/r-GO (Alli et al., 2022). The nanocomposite TiO_2/G was synthesized via thermal annealing (Hettiarachchi et al., 2023). Subsequently, transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and Raman techniques were utilized to characterize the synthesized nanomaterials (TiO_2, TiO_2/r-GO) and graphene (Hettiarachchi et al., 2023a). Scanning electron microscopy (SEM) was used to investigate the morphologies of graphene nanosheets.

2.3 Formulation and stability tests

FCO was formulated using virgin coconut oil (VCO) to improve its physicochemical properties for engine lubrication application (Hettiarachchi et al., 2023a). Dispersion stability is essential for a lubricant to ensure consistent performance in tribological applications (Liu et al., 2020). Nano-additives, graphene, and GO (0.1 wt.%) in 10 ml of 15W40, and FCO with nano-additives TiO_2/G and TiO_2/r-GO (0.1 wt.%) were sonicated separately for two hours, followed by further agitation for another two hours using a magnetic stirrer hotplate. A double-beam UV-Vis spectrophotometer was used to evaluate the absorption stability of blended nanofluids through optical absorbance spectroscopy. Samples were examined at 0, 24, 48, and 72 hours after blending and continued weekly for up to five weeks (Bhatt et al., 2009).

2.4 Performance tests

Friction tests on the above samples were performed for 25 load-velocity combinations using a Linear Reciprocating Tribometer (LRT) test rig, following ASTM G181-11 guidelines (Hettiarachchi et al., 2023a). Piston ring and cylinder liner segments of an ICE were used as test specimens to investigate the lubricity of sample blends at 140 °C and compare them with the reference oil 15W40. SEM micrographs were used to analyze the wear scars of the test specimens after the friction tests.

3 RESULTS AND DISCUSSION

3.1 Characterization of nanoparticles:

TEM and SAED analyses revealed that the nanocomposites TiO_2/G and TiO_2/r-GO are in the 2D scale based on the observed average particle sizes and lattice fringe spacing (d) of graphene sheets (TiO_2/G – 14.00 ± 0.30 nm and d = 0.38 ± 0.003 nm; TiO_2/r-GO – 10.00 ± 0.3 nm and d = 0.037 ± 0.002 nm). A lateral dimension of 319.0 ± 50 nm with d = 0.33 ± 0.004 nm was observed for the graphene nanosheets.
The XRD patterns observed for the synthesized nanoparticles confirmed the presence of graphene and the nanocomposites TiO_2/G and TiO_2/r-GO (Nguyen et al., 2022). Raman spectra of the synthesized nanomaterials also confirmed that the atomic bonding and geometrical patterns match the established data of graphene, and TiO_2/G and TiO_2/r-GO nanocomposites (Hettiarachchi et al., 2023; Baragau et al., 2020).

3.2 Dispersion stability of formulated nano lubricants

The spectral absorbency test results for samples based on 15W40 containing nano-additives G and GO confirm that the blend with GO is more stable than the blend with G. The functional groups (C=O, -COOH, -OH) attached to GO may have been functionalized with long-chain high molecular weight hydrocarbon molecules, each containing over 30 carbon atoms of 15W40, which could be the hypothesis affecting this result (Stachowiak & Batchelor, 2014).
The variation in UV-Vis absorbance measurements of the above samples with G additives shows a sharp reduction in absorbance from 0 h to 72 hours. It remained stable thereafter throughout the 5-week testing period. The sample with GO additives exhibits minor agglomeration during the initial 72 hours but displays enhanced dispersion stability thereafter. Perhaps, solutions become stable after the sedimentation of surplus quantities that are not soluble in 15W40 (Hao, 2005) (Figure 1). The results further validated the evidence of the observed stability test results.

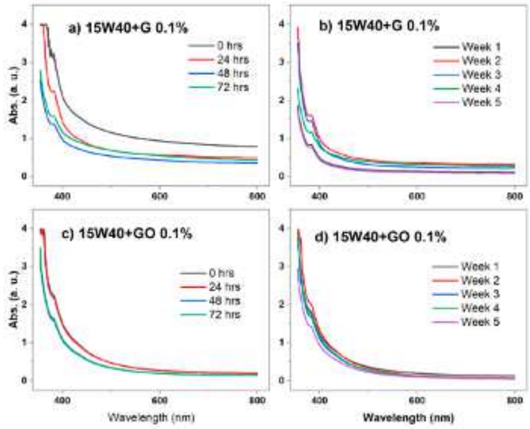

Figure 1. Overlayed UV-Vis spectra for 15W40-based samples having G and GO nano additives, a) & c) 0-72 h overlay in 24 h intervals and b) & d) 5 weeks overlay in weekly intervals.

Optical absorbance spectra for the FCO-based sample containing TiO_2/r-GO as nano-additives revealed a remarkable dispersion stability compared to FCO with TiO_2/G samples. The capability of oxygen functional groups of r-GO to keep nanoparticles dispersed within the solution is further supported by these results, accordingly confirming the proposed hypothesis with the above UV-Vis findings. Illustration of poor dispersion stability of samples containing TiO_2/G nano-additive, compared to the sample with TiO_2/r-GO nano-additives, demonstrates the potential of r-GO for creating a stable and homogeneous solution.

The results of absorbance vs. time analysis for both samples exhibited different degrees of sedimentation during the 0–72 h period, following consistent colloidal stability throughout the experiment range (Figure 2). The result of the stability observation test confirmed this further.

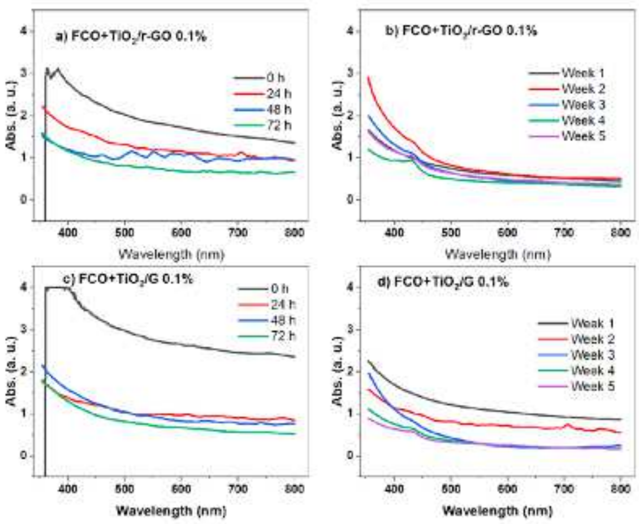

Figure 2. Overlaid optical absorbance spectra for FCO-based samples containing TiO_2/r-GO and TiO_2/G nano-additives: (a) & (c) 0–72 h overlay in 24 h intervals, and (b) & (d) 5 weeks overlay in weekly intervals.

3.3 Performance tests

The analysis of the coefficient of friction (COF) over time for the reference oil (15W40) and 15W40-based samples containing nano-additives G and GO indicates that the sample with GO demonstrates superior effectiveness in reducing friction compared to both the sample with G and the reference oil (15W40). Notably, the maximum COF reduction achieved was 72% for the combination of 200 N/50 Hz, with an average reduction of 26% for all 25 frequency/load combinations, compared to 15W40. In contrast, the sample containing G additives showed a maximum reduction of 42% and an average reduction of 17% in COF, relative to 15W40. As observed via UV-Vis analyses, the dispersion stability of GO has improved compared to G in the solution. It is presumed that the interactions of carboxyl or carbonyl functional groups on the GO surface with the sliding substrate, reducing asperity contacts, have affected this tribological improvement, because of the ability of GO nanoparticles to remain in the solution (Gupta et al., 2017).

From the results of tribological tests for the formulations containing FCO and TiO_2/G and TiO_2/r-GO nanocomposites, it is evident that both the blended samples can reduce friction more than 15W40. A 58% and 54% maximum and 26% and 23% average COF reduction were observed for the samples FCO+TiO_2/G and FCO+TiO_2/r-GO, respectively, compared to the reference oil. Despite the better stability of the sample FCO+TiO_2/r-GO, the reason for showing slightly lesser COF than the sample FCO+TiO_2/G can be attributed to the formation of molecular clusters in solution due to bonding between FCO molecules and oxygen functional groups of r-GO, which requires further investigation.

3.4 Wear scar analysis

The SEM images of cylinder liner segments with samples containing GO and TiO_2/r-GO showed improved surface morphologies compared to those with G and TiO_2/G, indicating that the functional groups of GO and r-GO form a protective layer that reduces wear at the tribological interface.

4 CONCLUSION

Results of UV-Vis analyses confirm the colloidal stability achieved for 15W40+GO and FCO+ TiO_2/r-GO samples due to the functionalization of oxygen functional groups attached to GO or r-GO elements with molecular chains of the base stock. This highlights the importance of surface functionalization in generating either repulsive or attractive forces between molecular substrates in a solution. The long-chain molecular structure of 15W40 contributes to the stability of the GO and r-GO groups in the base stock compared to FCO. The varying degrees of sedimentation of the above samples after 72 hours of formulation confirm the importance of particle concentration for the colloidal stability of a solution. These findings support the use of GO and r-GO functionalized additives in both mineral- and bio-based lubricants to enhance engine performance.

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