

# The Addition of Graphene Oxide to Enhance the Photo-Thermal Performance of a Premier Organic Heat Transfer Oil

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**Abstract:** The present study investigated the improvement in photothermal response and temperature enhancement of a commercially available organic thermal oil when small quantities of graphene oxide (0.1 to 0.3% w/v) were added. Characterisation studies revealed the ultrasonic processing procedure did not change the chemical composition of the organic oil, which was found to be thermally stable up to 175 °C before complete decomposition at 315 °C. When the GO-based fluids were exposed to a solar irradiance of 985 Wm<sup>-2</sup>, the temperature enhancements achieved over the exposure period of 20 minutes typically ranged from 42.4 to 43.2%. The temperature enhancements achieved indicate the GO-based fluids have the potential to be used in direct-absorption solar collectors for improved performance.

**Keywords:** Graphene Oxide, Photo-Thermal, Direct-Absorption, Solar Collectors

## 1. Introduction

Solar irradiation falling on the Earth's surface is the largest source of renewable energy that is readily available for collection, concentrating, and converting into other useful forms of energy. In recent years, direct-absorption solar collectors (DASCs) have attracted considerable research interest, since the collector's working fluid directly absorbs incident solar irradiation. Direct-absorption minimizes heat losses by reducing temperature differences between the absorber and the working fluid, which significantly enhances solar energy conversion [1]. Thus, delivering an alternative renewable energy system, which can assist in reducing the detrimental effects of carbon dioxide emissions and global warming [2, 3]. Importantly, working fluids that function as both absorber and transfer medium are critical for the performance of DASCs. Therefore, developing new or modifying existing working fluids to improve their photo-thermal properties is highly desirable to enhance the performance DASCs [4, 5]. The inclusion of low concentrations of well dispersed particles in traditional working fluids can significantly enhance their thermo-physical properties [6, 7]. However, the inclusion of large particles in working fluids has resulted in sedimentation, increased flow resistance, accumulation and blockage of small flow channels that result in higher system pressure drops [8, 9]. Because of these shortcomings, particle addition has failed to gain widespread acceptance. However, using low concentrations of nanomaterials in fluids can improve their thermal properties without the abovementioned shortcomings [10]. In recent years, studies have evaluated the

performance of fluids containing small quantities of carbon-based nanomaterials like graphite, graphene and graphene oxide. [11, 12]. The present work evaluated the photo-thermal performance of a commercially available heat transfer oil, Therminol 66<sup>®</sup> [13], when small quantities of graphene oxide (0.1 to 0.3% w/v) were added.

## 2. Materials and methods

### 2.1. Chemicals and materials

Graphene oxide powder (product number: GNOS0010) was purchased from ACS Materials, LLC (Pasadena, California, USA). While Therminol 66<sup>®</sup> was manufactured by Eastman Chemical (Kingsport, Tennessee, USA). All materials were used without further purification.

### 2.2. Preparation of graphene oxide-based Therminol 66<sup>®</sup> fluids

Three solution mixtures were prepared to produce the 0.1%, 0.2% and 0.3% (w/v) GO-based fluids. Initially, 1 ml of oil (Therminol 66<sup>®</sup>) was placed into the mortar and then 0.1 g of GO was added. This was followed by the mixture being ground with a pestle for five minutes to generate a smooth paste. The paste was then added to a 99 ml solution of oil. Similarly, the 0.2% and 0.3% (w/v) mixtures were prepared and added to oil solutions 98 ml and 97 ml respectively. All solutions were then sonicated for 10 minutes using an ultrasonic processor (Hielscher UP400S) set at a power level of 400 W. After processing, the resulting brown solutions were stored at room temperature before being characterised and used in the photo-thermal studies.



### 2.3. Characterization Techniques

A JEOL JCM-6000, NeoScope™ scanning electron microscope was used to produce images to determine particle size and shape of the supplied GO powders. While a Tecnai G2, FEI, (Electron Optics, USA) transmission electron microscope operating at 100 kV was used to study size and shape of individual GO flakes produced after processing. While atomic force microscopy was used to determine the three-dimensional shape and thickness of individual GO flakes using a Park systems NX10 (Park System Corp., Suwon, Korea). Imaging was done in tapping mode using a standard probe (OMCL-AC160TS) with the scan rate set to 0.6 Hz. A UV-Visible spectrophotometer (Varian Cary 50 series version 3) was used to examine the absorbance of the fluids. Fourier transform infrared spectroscopy (FT-IR) studies examined the chemical composition of Therminol 66® during processing. A PerkinElmer FT-IR/NIR Spectrometer Frontier with Universal signal bounce Diamond ATR attachment was used to collect spectra over a scanning range from 400 to 4000  $\text{cm}^{-1}$  with a resolution step of 1  $\text{cm}^{-1}$ . Thermo-gravimetric analysis (TGA) was carried out to determine the thermal stability of the GO-based fluids using a Perkin Elmer simultaneous thermal analyser STA 8000. Thermal stability was carried out in air with a flow rate of 20  $\text{ml min}^{-1}$ . The temperature range started at 30 °C and increased to 1000 °C at a heating rate of 25 °C  $\text{min}^{-1}$ .

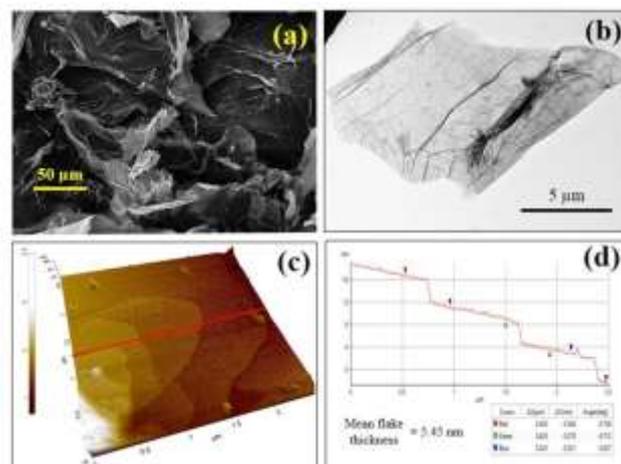
### 2.4. Photo-thermal and temperature enhancement measurements

Photo-thermal response measurements were carried out in an in-house solar simulator. A Philips 13096 ELH (120V, 300W-G5D) bulb supplied the light. The simulator was adjusted and calibrated using a LI-200 R Pyranometer to generate an irradiance of 985  $\text{Wm}^{-2}$  at 25 cm from the light source. The respective GO-based fluid samples (25 g) were placed in a glass petri dish (100 mm OD & 20 mm in height) fitted with a glass cover. Masses were determined using a laboratory balance (Ohrus pioneer PA214C analytical balance). Temperature measurements were taken at 5, 10, 15 and 20 minutes. Measurements were taken using a Digitech QM-1600 meter (thermocouple inserted into the fluid), while thermal images were recorded using a hand held thermal camera (Fluke Ti 25). Measurements were carried out in triplicate, with the mean value being used. Room temperature remained at 25 °C during the measurement period.

### 3. Results and discussions

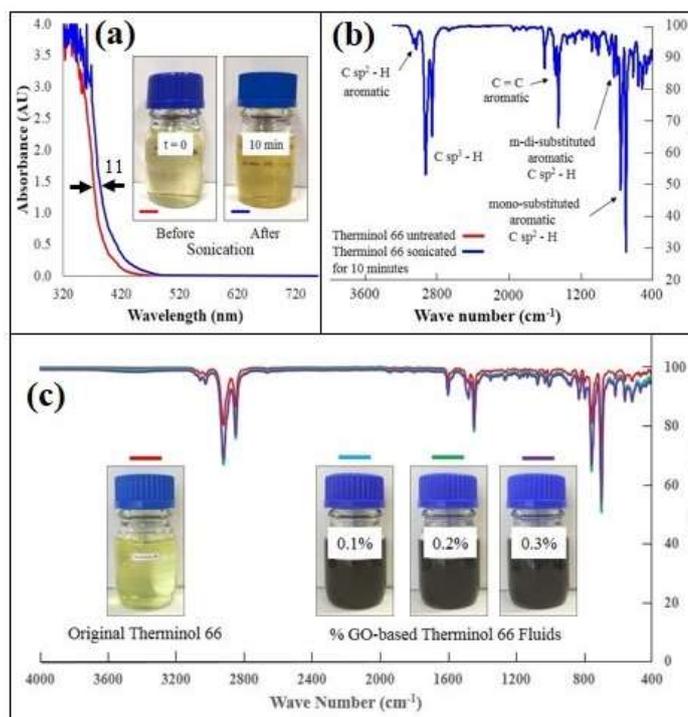
A representative SEM image of initial GO powder can be seen in Fig. 1(a). The powder is agglomerated and has large numbers of folding micrometre scale sheets that also show surface wrinkling. Fig. 1 (b) presents a TEM image of a well dispersed and transparent flake of GO produced after processing.

Fig. 1 (c) presents an AFM analysis of several flakes along the red scan line. Analysis of the scan gave a mean flake thickness of 5.45 nm, as seen in Fig 1 (d).



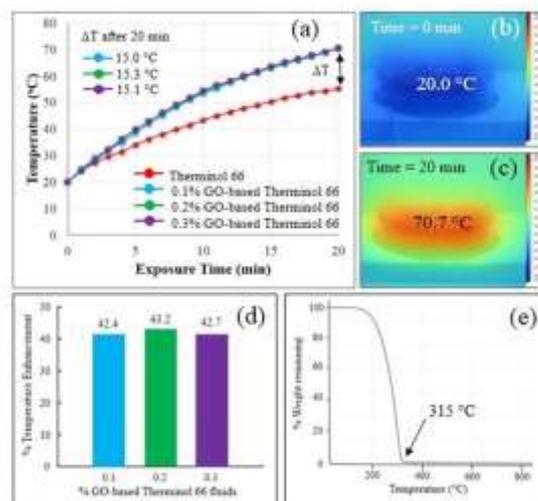
**Fig.1.** Characterisation studies of GO flakes (a) SEM of supplied GO powder, (b) TEM of a processed GO flake, (c) AFM scan of several GO flakes and (d) flake thickness analysis.

The influence of ultrasonic processing on Therminol 66® was investigated, since the oil changed from pale yellow to a darker shade of yellow after 10 minutes, as seen in Fig. 2 (a). UV-Visible spectroscopy revealed the yellowing of the oil caused the absorption edge to move to the right by 11 nm at a wavelength of 380 nm. A similar result was also reported by Grirate *et al.* while investigating aged Therminol 66® at elevated temperatures [14]. Since colour changes can indicate decomposition or oxidation, FTIR analysis was undertaken to assess the oils stability after ultrasonic processing. The resulting spectra showed no oxidation, since there were no hydroxyl or carbonyl bands present. The before and after spectra, when overlaid are a perfect match and only show the oils chemical composition as seen in Fig. 2 (b). FTIR analysis also showed the addition of GO did not change the chemical composition of the oil as seen in Fig. 2 (c). Also, increasing GO content darkened and reduced the transmission of light. For instance, at 700  $\text{cm}^{-1}$ , the light transmission of pure oil was 72%, but for the 0.3% GO-based fluid it was reduced to 54%. While the photo-thermal response results revealed the addition of small amounts of GO can have a significant influence on the degree of response as seen in Fig. 3 (a). This equated to significant temperature enhancements (Fig. 3 (d)), with the highest being 43.2% for the 0.2% GO-based fluid.



**Fig. 2.** (a) UV-Visible spectroscopy of oil before and after ultrasonic treatment, (b) FTIR analysis of chemical composition of oil before and after ultrasonic treatment, (c) FTIR analysis and % optical transmission of GO-based oils (0.1%, 0.2% and 0.3%).

Thermal stability was also evaluated and a representative thermograph for the 0.3% GO-based fluid is presented in Fig. 3 (e). Characteristically, all fluids had a single-step weight loss pattern, with decomposition starting at around 175 °C and ending with complete decomposition at about 315 °C. The final decomposition temperature was lower than the 345 °C specified by the manufacture [13]. The lower temperature was attributed to the open system configuration used during testing, which exposed the fluids to oxygen and hastened the degradation reaction. Considering the results of the present work, the addition of small quantities of GO nanomaterials (0.1 to 0.3% w/v) to the heat transfer oil significantly improved its photo-thermal performance. Also, the variation in photo-thermal response between the different GO quantities was small (~2%). Importantly, FTIR analysis revealed the ultrasonic assisted preparation procedure did not induce decomposition or oxidation of the oil. In addition, the inclusion of GO did not change the chemical structure of the oil. Thus, demonstrating the chemical stability and suitability of the oil for GO addition. Also, the GO-based fluids did not display particle agglomeration or sedimentation for over a period of three months. Thus, the outcomes indicate that this type of GO-based fluid is a suitable candidate for use in DASCs.



**Fig. 3.** (a) Photo-thermal response of GO-based fluids, (b) and (c) thermal images of a 0.3% GO-based fluid over a 20 min period, (d) thermal enhancement results for GO-based fluids, and (e) representative thermo-gravimetric analysis of a 0.3% GO-based fluid.

#### 4. Conclusion

The present work has shown the addition of small quantities of GO (0.1 to 0.3% w/v) to a commercially available organic thermal oil can significantly improve its photo-thermal response. The 43.2% temperature enhancement recorded for the 0.2% GO-based fluid, together with its stable fluid properties indicates that it can be used in solar thermal applications like DASCs.

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