Thermal Conductivity of Ethylene Glycol and Propylene Glycol Nanofluids with Boron Nitride Nano-barbs

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ARTICLE

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This study investigates the potential of composite allotrope boron nitride nanobarbs (BNNBs) as nanoparticles for enhancing the thermal conductivity of nanofluids based on mixtures of ethylene glycol and propylene glycol with water. BNNBs are allotrope composites composed of boron nitride nanotube cores with walls decorated with attached hexagonal boron nitride crystals, creating a jagged morphology that facilitates the formation of a connected network and contributes to the enhancement of thermal conductivity in nanofluids. BNNBs exhibit high thermal conductivity due to efficient phonon transfer and electrical insulating properties owing to a wide bandgap. The effect of BNNB concentration in carrier fluids on nanofluid thermal conductivity was investigated by introducing BNNBs into ethylene glycol-water and propylene glycol-water mixtures at 0 - 10 wt %. The results showed that BNNBs enhanced thermal conductivity of carrier fluids up to 45%, and the enhancement was proportional to the concentration of BNNBs in the carrier fluid. The study also investigated the dispersion stability of BNNBs in different solvents using Hansen Solubility Parameters, revealing that propylene glycol mixtures demonstrated better long-term stability compared to ethylene glycol mixtures. The findings suggest that BNNBs have great potential for use as thermally conductive nanoparticles in nanofluids for various heat transfer applications. Future research should focus on enhancing the dispersion stability of BNNB nanofluids and exploring the influence of BNNB morphology on the thermal conductivity and other thermophysical properties of nanofluids.

Introduction

Heat transfer fluids are essential in various applications such as chemical processing, power generation, air-conditioning, and electronics cooling, to name a few [1, 2]. However, commonly used heat transfer fluids such as water, ethylene glycol, and propylene glycol exhibit poor heat transfer properties due to low thermal conductivity and environmental restrictions. The addition of thermally conductive nanoparticles to heat transfer fluids has been explored to enhance their heat transfer properties. While several nanomaterials have been studied and added to heat transfer fluids, metal nanoparticles could increase electrical conductivity, or nanoparticle addition can lead to an increase in the fluid's viscosity, which can lead to higher energy consumption of the pump, affecting industrial applications.

Boron nitride nanoparticles (BNNPs) have recently gained significant attention due to their excellent thermal conductivity and electrical insulating properties [3]. In particular, boron nitride nanotubes (BNNTs) and hexagonal boron nitride (h-BN) have been extensively studied for their thermal properties. The thermal conductivity of boron nitride is much higher than metals and ceramics at room temperature, approximately 400 W m^{-1} K^{-1}. In this work, we introduce decorated boron nitride nanotubes, or "nano-barbs" (BNNBs), as nanoparticles for producing a thermally conductive nanofluid. These BNNBs are mixed-allotrope nanoparticles of BNNTs and h-BN crystallites, which offer significantly higher specific surface area compared to BNNTs or h-BN alone. The nano-barbs consist of BNNT cores decorated with a conformal but randomly oriented shell of h-BN crystals attached to the BNNT walls, creating a unique and new material with the potential to transfer heat in all direction more efficiently than the lateral heat conduction of BNNTs and h-BN [3]. We investigate the effect of BNNB concentration in ethylene glycol-water and propylene glycol-water mixtures on nanofluid thermal conductivity, and report that the BNNBs enhance thermal conductivity by up to 60%, with an improvement proportional to the BNNB concentration. We also report the viscosity of the carrier fluids at different temperatures and the BNNB dispersion stability. Our study demonstrates the potential of BNNBs as thermally conductive nanoparticles for various heat transfer applications and provides insights into the relationship between BNNB concentration and nanofluid thermal conductivity.

Commonly used heat transfer fluids, such as water, ethylene glycol, and engine oil, have poor heat transfer properties due to low thermal conductivity and environmental restrictions. Water, the most common and cost-effective cooling agent, has a high specific heat capacity and good transport properties.

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However, water use is limited by its freezing temperature and boiling temperatures, but more importantly, the propensity for water to gain ions and increase electrical conductivity. Other cooling agents, such as ethylene glycol and propylene glycol, are often used in place of water; however, they have a higher viscosity than water and require higher power pumps.

Currently, ethylene-glycol and propylene-glycol mixtures with water are used as heat transfer fluids in building heating, electronics, ventilation, and air-conditioning systems. Adding various ratios of propylene glycol and ethylene glycol to water lowers its freezing point and raises its boiling temperature. As a result, the operational temperature range of applications is expanded [4]. Other advantages of glycol-water mixtures include the prevention of acid degradation, corrosion, and the growth of nearly all microorganisms. The thermal conductivity of these glycol-water mixtures is lower than that of water. So, methods to improve thermal properties without compromising other beneficial properties are required. Thermally conductive nanomaterials dispersed in glycol-water mixtures create nanofluids, which have been shown to improve their thermal properties.

A wide variety of nanomaterials and nanoparticles with good thermal transport properties, such as Fe3O4, SiO2 [5], CuO [6], Al203 [7], metal-organic frameworks (MOFs), carbon nanotubes [8, 9], and boron nitride nano-(0D, 1D, 2D) [10-13], are regularly studied and added to heat transfer fluids to improve the heat transfer efficiency. Many of these additions to nanofluids do not significantly affect the fluid's rheological properties [12]. The rheological properties of the nanofluid, particularly viscosity, are important in determining the pumping power of equipment required for nanofluid applications, such as heat exchangers, because a significant increase in viscosity will increase the power required for pumping, resulting in a higher energy consumption of the pump. To meet industrial requirements, nanofluids should have low particle loading but high thermal properties, favourable rheological properties and flow behaviour, and excellent stability over a broad range of temperatures[14]. Much of the research is focused on producing stable systems of high thermal conductivity nanofluids with well-dispersed nanoparticles [15].

Boron nitride nanoparticles (BNNPs) like boron nitride nanotubes (BNNTs) and hexagonal boron nitride sheets (h-BN) with a similar structure and mechanical properties to their carbon counterparts have received significant interest in recent years due to their electrically insulating property [16]. The wide bandgap of BNNPs makes them electrically insulating materials, while the high phonon transfer along their atomic lattice makes them excellent thermal conductors. Recently, BNNPs have been used to synthesize nanofluids showing improved thermal conductivity [11, 17, 18]. Li et al. [19] reported abnormally high thermal conductivity enhancement for nanofluids containing BNNPs of 140nm compared to 70nm size. Notably, this work demonstrates the influence of BNNP size and stabilizing surfactant on the thermal conductivity of nanofluids. Taha-Tijerina et al. compared the similarities between h-BN and graphene [16]. In their work, the structurally analogous nanoparticles were dispersed in mineral oil and evaluated for use in thermal management and lubrication. Krishnam et al.[20] studied BNNPs with several surfactants, SDS, CTAB and Tween 80, to produce BN-based nanofluids. Unexpectedly, they concluded that BN-nanofluids combined with surfactants were less stable than BN-nanofluids without surfactant. These findings have influenced this work leading us to study mixed allotrope BNNPs previously unreported for nanofluid development.

In this study, BNNPs in the form of "nano-barbs" are dispersed in ethylene glycol (EG)- and propylene glycol (PG)-water mixtures to produce nanofluids with high thermal conductivity. Boron nitride nano-barbs (BNNBs) are mixed-allotrope nanoparticles of BNNTs and h-BN crystallites. BNNBs are effectively BNNTs decorated with a conformal but randomly oriented shell of h-BN crystals attached to the BNNT walls. These h-BN crystals will be considered impurities in research requiring pure BNNT, necessitating several and intensive purification processes [21]. The BNNB are used to create nanofluids consisting of 0.01 to 10 wt % BNNBs in EG-water and PG-water-based fluids. The glycol: water ratios were 100:0, 75:25, 50:50, and 25:75. The thermal conductivity of each nanofluid was measured at 40 °C using a hot disk thermal analyzer. The viscosity of the carrier fluids is reported at 5 °C, 40 °C, and 70 °C, and the BNNB dispersion stability was evaluated using estimated turbidity from absorption spectroscopy. The influence of BNNB concentration on nanofluid viscosity and thermal conductivity was studied and discussed.

Experimental

Materials

Mono ethylene glycol (99%) was purchased from UCA- Uniclean America and used without further purification. Propylene glycol (99.9% Pure USP Food Grade) bought from Fisher Scientific BNNBs were supplied by BNNano, inc. as 10 wt % dispersions in ethylene glycol and propylene glycol. No additional purification was conducted on received materials. Nanofluids were dispersed and sonicated using a Hielscher ultrasonic UP200st set at a continuous power of 20 W for 5 min, and temperature was not controlled or monitored during sonication. The BNNB nanoparticles' morphology was studied using a transmission electron microscope (TEM) (JEOL 2100PLUS) and a scanning electron microscope (SEM 200). The FTIR characterization was carried out on an Agilent diamond ATR FTIR from 400 to 4000 cm^{-1}. The dried BNNB samples were directly placed and pressed onto a diamond ATR crystal. Thermal conductivity measurements were performed with a hot disk thermal constant analyzer (TPS 2500).

Preparation of BNNB nanofluids

Ethylene glycol-water and propylene glycol-water mixtures were prepared by mixing each glycol to water solution in volumetric 100:0, 75:25,50:50, and 25:75 glycol: water ratios. The ethylene glycol- and propylene glycol- deionized water mixtures were shaken vigorously before use to ensure a homogenous solution. For the 100:0 glycol: water nanofluids, initial measurements of the as-received 10 wt % BNNB nanofluids were conducted before they were used in serial dilution to make nanofluids with concentrations from 0 to 10 wt % BNNBs. The dilution table is provided as supplemental information, SI 1. For the glycol: water ratios of 75:25, 50:50, and 25:75, aliquots of the as-received 10 wt % were diluted with pure glycol: water mixtures to create samples from 0 to 5 wt %. During each step of the serial dilutions, the previous stock was tip-probe sonicated for 5 minutes at 20 W before pipetting from the center of the dispersion to limit mass transfer errors due to precipitation of the BNNBs.

Characterization of BN Nano-barbs

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to visualize the morphology of the BNNB nanoparticles. Figure 2a) and (b) show the SEM images of the BNNB samples. The decorated mixed allotrope morphology of the BNNBs is represented in the TEM micrographs shown in Figure 2(c) and (d). From the SEM images (Figure 2a & b), the rough, irregular surface of the BNNBs is noticeable. The TEM provide more clarity on the rough morphology showing the conformal attachment of irregular h-BN particles to the surface of the BNNTs (Figure 2c & d). The average particle diameter observed appears to be approximately 50nm.

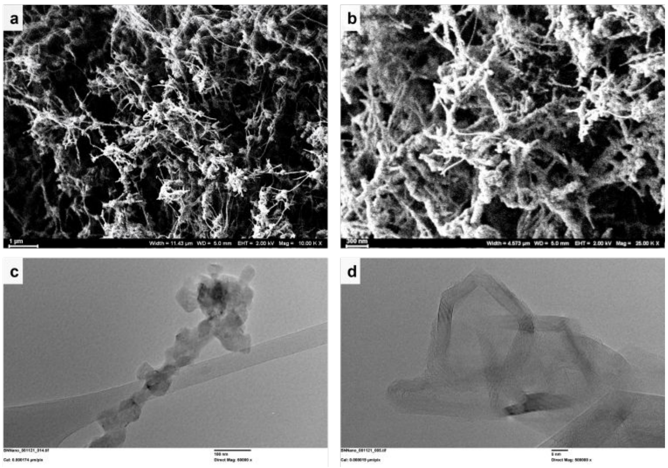

Figure 2: (a and b) SEM (c and d) TEM of Boron Nitride Nano-barbs

The FTIR spectroscopy in Figure 1 provides valuable information about the morphology of the BN nano barbs. In the low frequency region of the FTIR spectra, the hexagonal BN network of the nano-barbs exhibits distinctive structural vibrations. The spectra show a peak at 1369 cm^{-1} that corresponds to the two merged optical phonon modes, transverse optical (TO) and longitudinal (LO), which are caused by B-N stretching. It also shows another peak at 806 cm^{-1}, which indicates the out-of-plane buckling mode of the hexagonal plane, B-N bending[22]. The low out-of-plane to TO peaks ratio indicates the presence of a high content of nanotube structures [23].

Thermal conductivity Measurement

The nanofluid thermal conductivity was measured using a hot disk thermal constant analyzer which uses the Transient Plane Source (TPS) method [24] to determine the absolute thermal conductivity of a sample. This method relies on the use of a transiently heated plane sensor. The TPS method offers good accuracy (>5%), excellent repeatability, and requires only a small sample volume (~ 5 ml), and a short measurement time (< 30 seconds per measurement). The glycol-water BNNB nanofluids were measured at 40 °C.

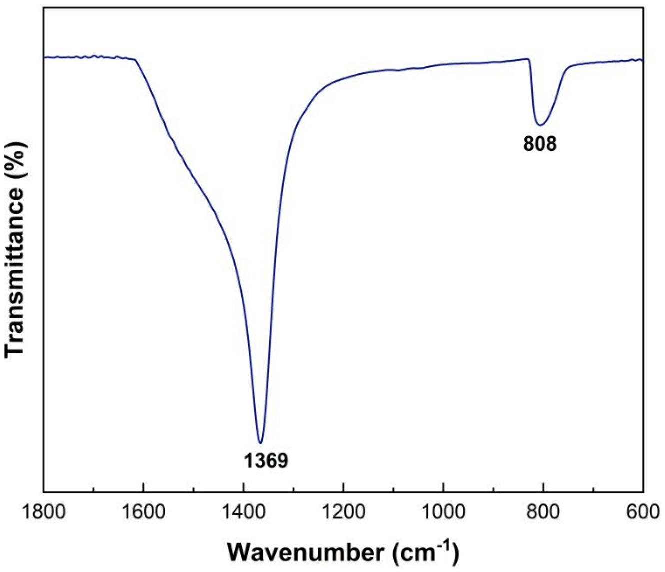

Figure 1: FTIR spectra of Boron Nitride Nano-barbs

The hot disk sensor consists of an electrically conducting double spiral pattern of 10-micron thick nickel foil and is insulated on both sides with thin sheets of mica or Kapton. Figure 3c is a photograph of the TPS sensor in Kapton. The hot disk sensor operates as a heat source, supplying constant power, and as the sample temperature sensor. The TPS is subjected to a heat pulse on one side, which generates a temperature gradient that moves through the TPS and subsequently enters the samples. The TPS records temperature data at different locations and times as the temperature gradient moves through it and the samples. After collating the temperature data obtained, the Hot Disk instrument determines the thermal conductivity of the sample and other thermal properties such as thermal diffusivity and specific heat. Initially, a custom liquid sample holder was utilized to establish the measurement of nanofluid thermal

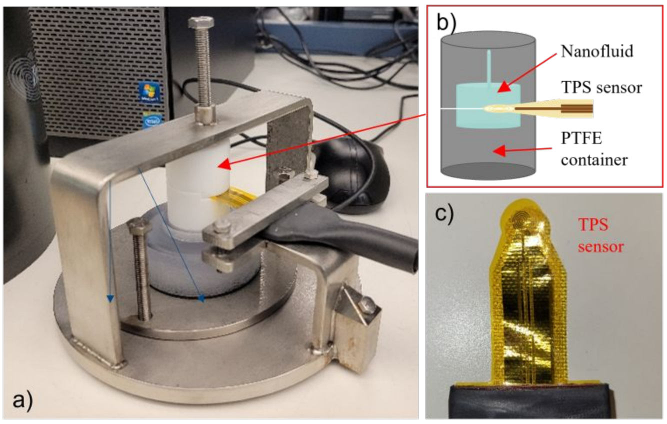

Figure 3: Hot disk thermal constant analyzer (a) Liquid sample TPS setup (b) Custom liquid sample container (c) TPS sensor

conductivity. Figure 3a displays the hot disk sensor that was integrated into the custom PTFE container. The setup consisted of two PTFE pieces that were used to sandwich the sensor, which was suspended in the middle of the container volume. When the container was filled, both sensor sides came into contact with the nanofluid sample (Figure 3). Typically, this custom PTFE setup with the sensor and sample is placed in a controlled temperature environment, such as an oven, for temperature measurements, aside from room temperature. However, due to the nature of the custom material, which prevents sufficient temperature interaction between the sample and controlled environment, this setup is commonly used for measurements at room temperature. Measurements at 40 °C, the sonicated sample is placed in a glass vial and put in a jacketed beaker that is temperature-controlled with a chiller. The TPS sensor is inserted into the sample so that the spiral part of the sensor is covered by the sample, and the sample is allowed to stabilize at the required temperature (0 or 40 °C). Several thermal conductivity measurements were conducted to account for variations caused by the instability of nanofluid samples. The measurements at 0 °C for the nanofluid samples were not performed due to the rapid settling of BNNB and the longer duration required to achieve a stable temperature.

Viscosity measurement

The viscosity of glycol carrier fluids and BNNB nanofluids was determined using an m-VROC viscometer (RheoSense Inc.) with a borosilicate glass measuring chip. This measuring chip has a rectangular slit flow channel with a uniform cross-section, requires only microliter sample volumes, and prevents contamination, evaporation, and free surface effects of the sample during measurement due to internal flow. During the measurement, the nanofluid samples were pushed at a constant flow rate through a 0.5mL syringe pump. The viscosities of each sample were measured at three different temperatures (5 °C, 40 °C, and 70 °C), and the shear rate range for most of the samples was between 400 and 2000 s^{-1}. Each measurement was repeated at least three times to ensure accuracy.

Result and Discussion

Carrier fluid

The thermal conductivity of the carrier fluids (mixtures of ethylene glycol or propylene glycol with varying amounts of distilled water) was measured as a function of temperature. The thermal conductivity of the carrier fluid increases as the water percent increases in the ethylene glycol/water mixture and propylene glycol/water mixture, as shown in Figure 4(a) and (b) for both measurements at 0°C and 40°C. Furthermore, the thermal conductivity measurement at 40 °C was higher than the measurement at 0°C, which is consistent with the findings of other authors [25, 26]. The effect of temperature on thermal conductivity becomes more noticeable as the water content in the glycol mixture increases.

Effect of BNNBs on thermal conductivity of carrier fluids

It is necessary to investigate the effect of these unique boron nitride nanoparticles on the thermal conductivity of the most commonly used fluids in heat transfer applications. It is also critical to comprehend how the concentration of BNNBs influences their dynamics and behavior in nanofluids. In this study, BNNBs in weight fractions ranging from 0.01% to 10% were dispersed in carrier fluids of ethylene- and propylene-glycol water mixtures, and the thermal conductivity of these solutions at 40 °C was measured. The resulting thermal conductivities of the nanofluids are graphically compared to those of the carrier fluids in **Error! Reference source not found.**. This figure show that the addition of BNNBs improved the thermal conductivity of the ethylene- and propylene-glycol water mixtures.

Error! Reference source not found.a depicts the thermal conductivity of prepared ethylene glycol/water nanofluids with weight fractions (0.01% –10%) of BNNBs. The addition of the BNNBs was effective in improving each carrier fluid’s thermal conductivity. As the concentration of the BNNB particles in the nanofluids increases, the thermal conductivity also increases. At 10 wt % BNNBs in ethylene glycol, the thermal conductivity increases to 0.37382 W m^{-1} K^{-1} at 40 °C. With an increase in

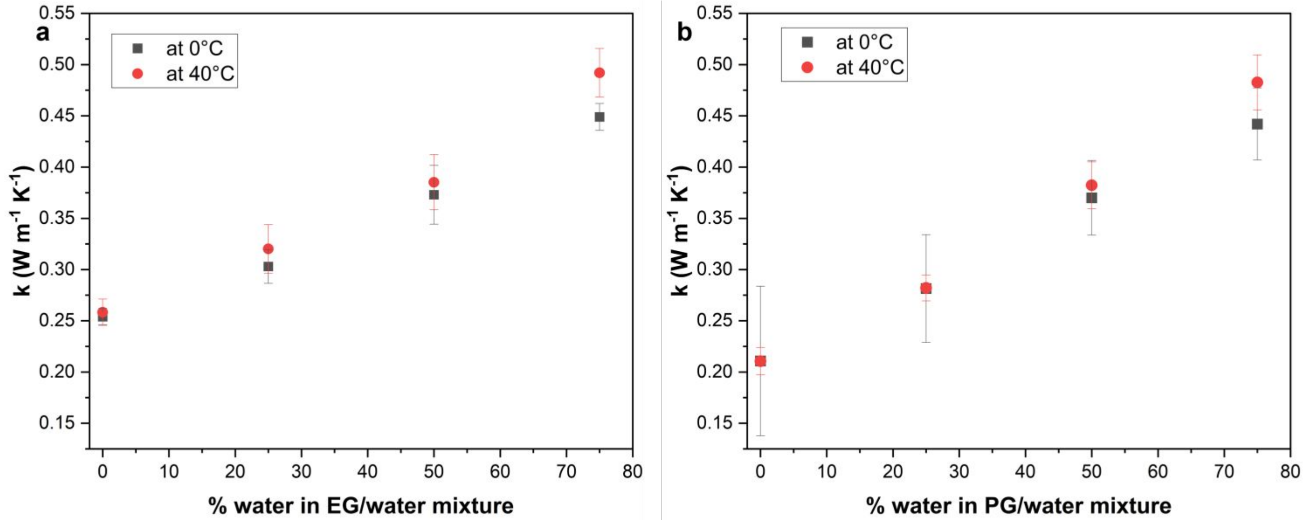

Figure 4: Thermal conductivity measurement of a. ethylene glycol/ water mixture b. propylene glycol/ water mixture

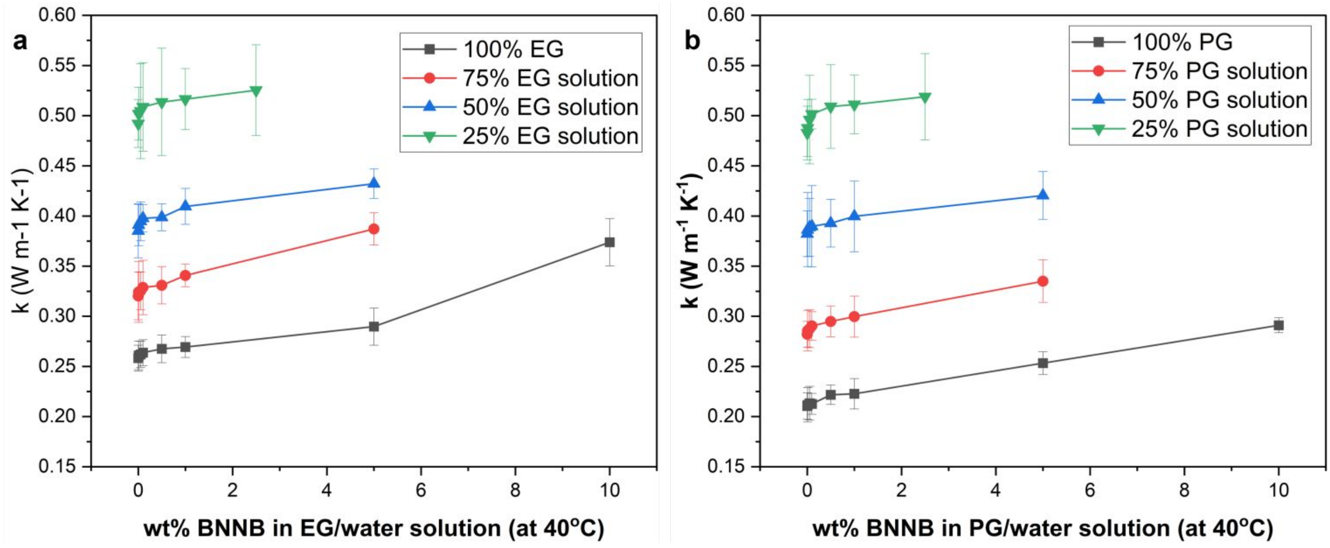

Figure 5 Thermal conductivity as a function of the glycol/water ratio and weight fraction (0.01% –10%) of BNNB at 40 °C for a. in ethylene glycol/water b. in propylene glycol/water

concentration, the jagged morphologies of the BNNBs increase the probability of forming a connected network through their contact, which results in a significant thermal conductivity increase.

Also measured was the thermal conductivity of the prepared BNNB in propylene glycol/water nanofluids. **Error! Reference source not found.**b shows the thermal conductivity obtained for the different propylene glycol/water mixture ratios with weight fraction (0.01% –10%) of BNNBs. The addition of the BNNB effectively improved each carrier fluid's thermal conductivity. The thermal conductivity also increases as the concentration of the BNNB particles in the nanofluids increases. The thermal conductivity increases to an average of 0.29101 W mK^{-1} at 40 °C for the max concentration of 10 **wt %** BNNB in propylene glycol.

Effects of BNNBs on Viscosity of carrier fluid

The viscosity of a fluid is an important rheological property that indicates its internal resistance to flow. This implies that the viscosity of nanofluids will be affected by the properties of the nanoparticles present, such as shape, size, concentration, and particle-molecule interaction. In this study, we measured the effective viscosity of our carrier fluids (ethylene- and propylene-glycol water mixtures) and BNNB nanofluids of varying concentrations at three temperatures: 5°C, 40°C, and 70°C. **SI 2** depicts the viscosity measurements of the base nanofluids at 5°C, 40°C, and 70°C graphically. The viscosity of the ethylene glycol and propylene glycol fluids decreased dramatically as the temperature increased from 5 °C to 40 °C to 70 °C. This decrease in viscosity is associated with an increase in the ease with which molecules move in relation to one another. At higher temperatures, the kinetic energy of the molecules increases while the strength of the intermolecular attractive force between the molecules decreases, allowing fluid flow with less resistance. Also, the viscosity of glycol fluids reduces upon adding water due to the low viscosity of water. From **SI 2**, it can be deduced that ethylene glycol-based nanofluids will be less viscous than propylene glycol-based nanofluids. Due to less flow restriction, ethylene glycol nanofluid will provide better heat transfer than propylene glycol nanofluid. However, due to its

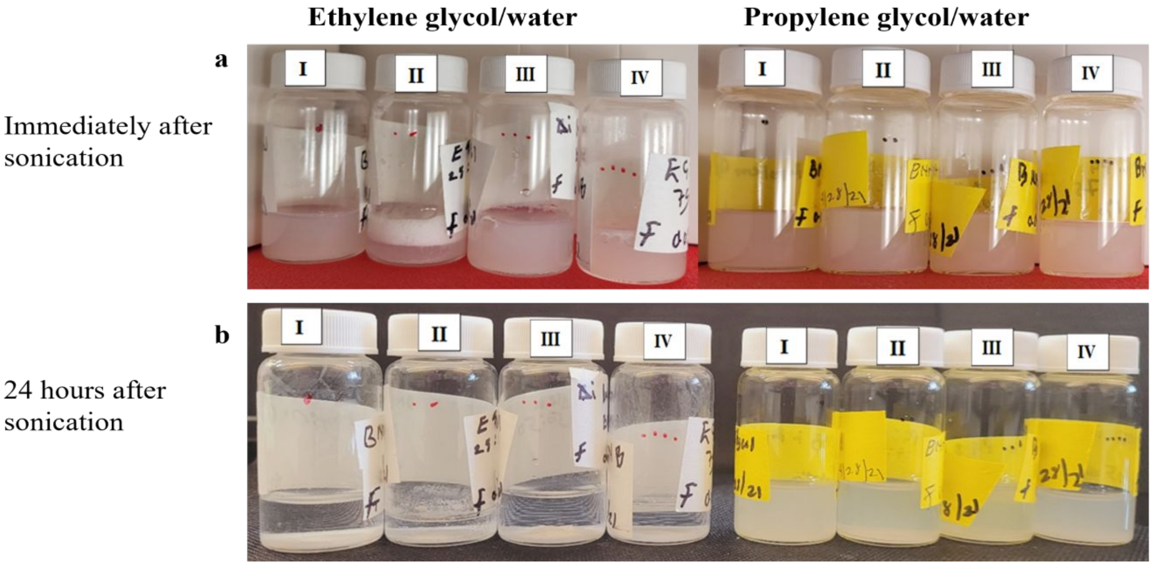

Figure 6: Image of EG/water and PG/water based BNNB nanofluids a. immediately after sonication b. 1 days after dispersion; I. pure glycol II 25% glycol III. 50% glycol IV. 75% glycol; left ethylene glycol/water (white label), right propylene glycol/water (yellow label).

high toxicity, ethylene glycol-based nanofluid cannot be used for applications in the open system, food, and pharmaceutical industries[27, 28]. Hence, propylene glycol-based nanofluids are used in applications involving food or potential contact with drinking water because they are nontoxic under normal conditions **[29]**.

The viscosity measurements for the EG and PG with water and BNNB nanofluids are included in SI **3** and SI **4**. As expected the viscosity of the nanofluids decreases with increasing temperature, and despite the poor stability viscosity slightly increases with increasing nanoparticle concentration. Increases in viscosity are a result of the interaction between the nanoparticles and the molecules of the carrier liquid of the nanofluid as concentrations increase [30, 31]. However, as the concentration of nanoparticles in the glycol-water nanofluids increased, the complication due to dispersion stability increased. The m-VROC viscometer is reads viscosity by measuring the pressure drop as a test liquid flows through a rectangular microfluidic channel. During temperature equilibration the settling of unstable BNNB particles clog the viscometer channel. As a result, measuring the temperature-dependent viscosity of nanofluids with concentrations greater than 0.05 wt % for propylene glycol nanofluids and 0.5 wt % for ethylene glycol nanofluids proved difficult. While the viscosity measurements of the measured samples deviate slightly from the expected linear correlation, we can observe the increase in viscosity in BNNB addition. Irregularities can be attributed to the rapid agglomeration and instability of BNNB nanoparticles within our nanofluid formulation.

Evaluating the Stability of unstabilized BNNB Nanofluids

Visual Measurement

Nanofluid thermo-physical properties (like; thermal conductivity and viscosity) depend on its stability [32]. Hence, the poor stability of nanofluid can impede its performance in applications. Figure 6 depicts a physical test to determine the dispersion stability of BNNBs in ethylene glycol/water mixtures and propylene glycol/water mixtures. The EG/water and PG/water nanofluids containing 0.05 wt % of BNNB were sonicated for 5 minutes at 20 W to disperse the BNNB particles effectively. Dispersions in the ethylene glycol mixtures were unstable, apparent as the BNNB particles started settling minutes after sonication. Propylene glycol mixtures showed significantly better long-term stability compared to the ethylene glycol mixtures, as evidenced by the persistent cloudiness of the solutions with much less settled BNNBs at the base. The cloudiness is evidence that unstabilized PG-BNNB nanofluids may be viable. In the absence of stabilizer heat transfer through a percolation network in BN based nanofluids would not be retarded by additional polymer or surfactant.

Turbidity α Absorbance

Turbidity is a measure of the cloudiness or haziness of a fluid that arises from the presence of particles, suspended solids, which are often too small to be seen with the naked eye. However, turbidimetry can more generally be used to measure the presence of solid particles in a non-homogenous solution. Turbidity readings can be effected by several parameters, including particle number, size, optical properties, width of particle size distribution, and particle shape, while particle number and size have the most significant impact [33]. Because of differences in instrument design, measurements can vary between devices. Typically, to make a quantitative turbidity measurement an instrument should be calibrated to a turbidity standard.

While a nephelometer is commonly used to measure turbidity by detecting the amount of light scattered by a light source, several studies have demonstrated the use of absorbance measurements from UV-VIS spectrometers to estimate solution turbidity [34, 35]. They have established a relationship between turbidity and absorbance shown by Equation 1, where turbidity is effectively proportional to absorbance by a proportionality factor and the inverse of the optical path length. By using absorbance measurements, relative turbidity measurements can be used for a set of internally consistent samples. As such, as equivalent particle dispersions are aggregating in a set of

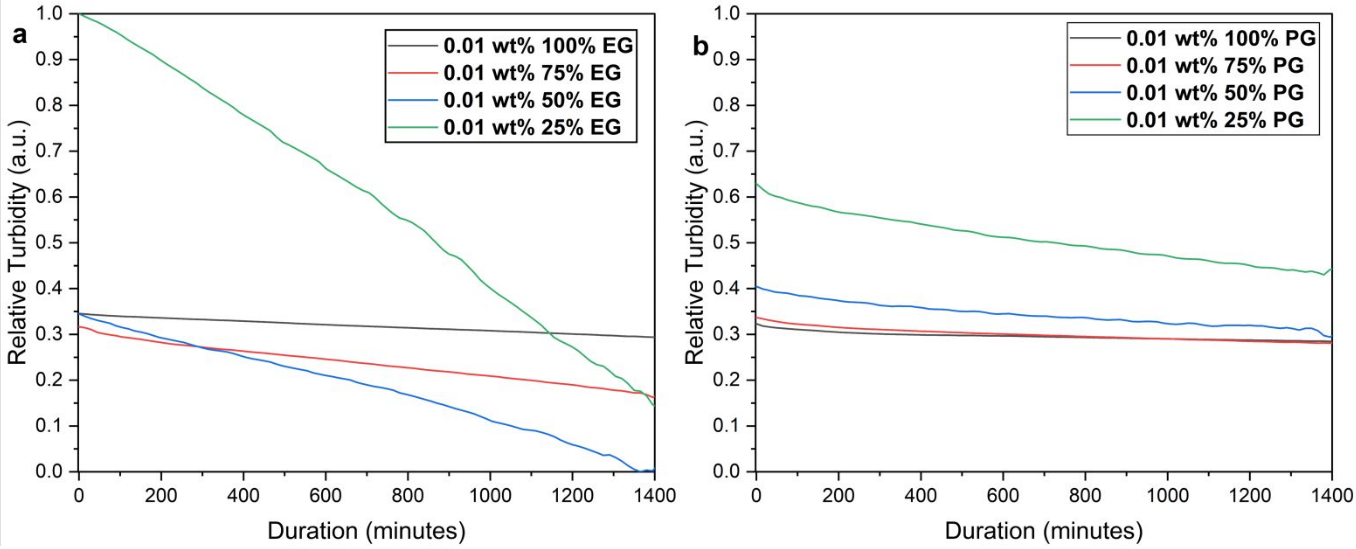

Figure 7: Relative turbidity of the BNNB nanofluids. Initial measurements start approximately 5 min after nanofluid formation. a. EG/Water based BNNB nanofluids against Time b. PG/Water based BNNB nanofluids against Time.

solutions, the relative particle dispersion stability can be measured as the rate of change of the turbidity of each solution.

$$\text{Turbidity} = (2.3 * A)/ L \qquad \text{equation 1. [35]}$$

Where A = absorbance and L = optical path length (1 cm - diameter of cuvette used).

A UV-vis spectrophotometer was used to measure the turbidity of EG/water and PG/water BNNB nanofluid solutions. In this study we use equation 1 to convert absorption values into turbidity. Figure 7 illustrates the rate of change of relative turbidity versus time for each sample, as measured by UV-Vis spectrophotometer at 475 nm over a 24-hour period, then converted to turbidity using equation 1. These data offer insight into the relative stability of the nanofluids compared to the composition of the carrier fluid. Agglomeration and settling of nanoparticles in the fluids is a predominant characteristic of this nanofluid composition, an instability that increases with the increase in water content.

It is important to note that the BNNB nanofluids exhibit significant instability in the first several minutes. The instability manifests as a rapid agglomeration during the first few minutes after formation. UV-vis measurements begin approximately 5 min after the nanofluids are formed, which is likely the cause of the variation of the initial values of the "un"-normalized turbidity. Due to inherent uncertainty in our manual procedural variation the initial turbidity cannot be used as an accurate measure for early dispersion stability. However, the relative rate of turbidity change (slopes) of the samples presented in Figure 7 can be directly compared and can serve as indicators of long term BNNB stability in each nanofluid dispersion.

We interpret the decreasing turbidity of each sample over time as a measure of aggregation and sedimentation of the BNNBs from the fluids. The faster BNNBs aggregate and sediment from a nanofluid is a direct indicator of dispersion stability, which is proportional to the rate of relative turbidity change. From our analysis we can see a similar distinct trend in long term stability versus the solvent composition for both the EG and PG-based nanofluids. For both EG and PG-based fluids as the water content increases the rate of relative turbidity change increases. The magnitude of the turbidity rates-of-change for EG and PG are different, where PG-based nanofluids all exhibit flatter slopes compared to analogous EG-based fluids. This observation is consistent with expectations proportional to the viscosity differences of EG and PG at the concentrations measured in Figures SI **3** and SI **4** . The lower viscosity of EG nanofluids permits faster Brownian motion of BNNB nanoparticles, leading to quicker aggregation sedimentation over time. This effect is amplified as the water content is increased both by the viscosity effect, and the increased polarity of the nanofluid carrier fluid decreasing unstabilized BNNB compatibility with the system.

Implications of Hansen Solubility Parameters on BNNB dispersion Stability

Hansen Solubility Parameters (HSP) are a set of three empirical values that quantify the solubility characteristics of a substance. These parameters were first introduced by Charles M. Hansen in 1967 [36] as a way to predict the solubility and miscibility of different materials. The three components of HSP are dispersion forces (δD), polar forces (δP), and hydrogen bonding forces (δH). They are instrumental in understanding the dispersion stability of nanoparticles in various solvents and predicting their behavior in complex mixtures.

Table 1. Hansen solubility parameters (HSP) of ethylene glycol, propylene glycol and boron nitride nanotubes (BNNTs)

	Hansen solubility parameters ($MPa^{0.5}$)		
	δD	δP	δH
Ethylene glycol [37, 38]	17	11	26
Propylene glycol [37]	16.8	9.4	23.3
Water [37]	15.1	20.4	42.3
BNNTs [38]	16.8	10.7	14.7
25% water in EG	16.5	13.1	30.1
25% water in PG	16.2	12.1	30.5

Table 1 contains the Hansen Solubility Parameters (HSP) of EG, PG, water, and BNNTs. The HSP of BNNTs have been rigorously determined by Castillo et al. [38] and are presented here for discussion purposes. Our BNNPs, as mentioned early, are allotrope composites of BNNTs and h-BN crystallites. This creates a challenge in our interpretation of HSP and prediction of stability due to an ongoing debate in the field about the hydrophilicity differences between h-BN and BNNTs. It has been observed that h-BN films are predominantly hydrophilic, exhibiting water contact angles around 55 degrees, while BNNTs have water contact angles in the superhydrophobic regime around 166 degrees [39]. These data suggest that h-BN have significantly higher hydrogen bonding character than BNNTs. The large hydrophilicity difference may simply be due to the higher density of "edge-based" chemical states in h-BN compared to BNNTs, where edges will be terminated in hydroxyl groups or amine hydrogen, and for BNNTs are only at the ends of tubes. From this conjecture we imagine that BNNBs would have similar dispersive HSP to BNNTs but slightly it higher hydrogen bonding contributions.

To predict the dispersion stability of BNNPs in EG and PG, we can calculate the differences in HSP values (ΔδD, ΔδP, and ΔδH) between BNNTs and the pure solvents. Generally, if the HSP values are closer together, the compatibility between the solute and solvent will be higher, leading to better dispersion stability. From Table 1 we can see that water has a significantly higher δP and δH than BNNTs, and when combined with EG or PG even at 25%, the δP and δH HSP are increased well above that of BNNTs. The addition of water increases the δP and δH values for both mixtures, so the BNNPs are expected to experience decreased dispersion stability in all water mixtures due to the larger differences in δP and δH values. In agreement with our observations, addition of water increased thermal conductivity and reduced viscosity, but results in a much higher likelihood of agglomeration or sedimentation of BNNPs in the mixtures. Between the two 25% water solutions, the 25% water in propylene glycol has a slightly lower ΔδP value, which might suggest marginally better compatibility with BNNPs compared to the 25% water in ethylene glycol mixture. However, overall, the dispersion stability of BNNPs in all water mixtures is expected to be lower compared to pure EG and PG. A complete description and set of calculations for blended HSP values in provided in SI.

Conclusions

In summary, our research on Boron Nitride Nanobarb (BNNB) nanofluids demonstrated a significant improvement in the thermal conductivity of ethylene glycol and propylene glycol-based water mixtures with the addition of BNNBs. The thermal conductivity of the carrier fluid increased with higher water content and temperature, while the BNNB addition further enhanced the conductivity. An increase in BNNB concentration led to a higher thermal conductivity, presumably due to the jagged morphologies of BNNBs, facilitating the formation of a connected network.

The viscosity of the carrier fluids decreased with temperature and showed a slight increase with the addition of BNNBs. Ethylene glycol-based nanofluids exhibited lower viscosity compared to propylene glycol-based nanofluids, indicating better heat transfer performance. However, ethylene glycol's high toxicity limits its applications in open systems, food, and pharmaceutical industries, while propylene glycol-based nanofluids are preferred due to their nontoxic nature.

Our investigation of BNNB dispersion stability revealed that ethylene glycol mixtures exhibited poor stability, while propylene glycol mixtures demonstrated better long-term stability. This finding supports the potential use of unstabilized PG-BNNB nanofluids in certain applications. However, rapid agglomeration and instability of BNNB nanoparticles in the nanofluid formulations were also observed, indicating that improving dispersion stability is crucial for the broader application of these materials.

Future research should focus on enhancing the dispersion stability of BNNB nanofluids by exploring different stabilizing agents, such as surfactants or polymers, or optimizing the dispersion method. Additionally, a detailed investigation of the influence of BNNB morphology on the thermal conductivity and other thermophysical properties of nanofluids would be beneficial for designing more efficient heat transfer fluids. Furthermore, a comprehensive understanding of the compatibility between BNNBs and various solvents, using Hansen Solubility Parameters, will aid in the development of stable and high-performance nanofluids for diverse applications.

Author Contributions

A.O. Maselugbo and J.R. Alston conceived the research; A.O. Maselugbo synthesized and characterized the thermal conductivity of samples and performed the theoretical calculations; A.O. Maselugbo and B.L. Sadiku wrote the paper; all authors discussed the results and revised the manuscript. J.R. Alston: conceptualization, supervision, project administration, resources, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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