

# Propylene Glycol-Water Based Titanium Carbonitride Nanofluids Designed For Heat Transfer Applications

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**Abstract** - This study aims to characterise new titanium carbonitride (TiCN) nanodispersions based on a mixture of propylene glycol and water at 20:80 mass ratio (PG:W). The temporal stability, thermal conductivity, isobaric heat capacity and dynamic viscosity of the samples were studied for different concentrations of TiCN. The dispersions were subjected to a stability treatment using poly(sodium 4-styrenesulfonate) (PSS) as surfactant with a PSS:TiCN mass ratio of 1:10. The samples showed good temporal stability after 15 days through a study of the evolution of the hydrodynamic size of the nanoparticles within the dispersion. Thermal conductivity was measured and a maximum enhancement of 4.7% was found for the TiCN(0.5 wt.)/PG:W 20:80 nanofluid. On the other hand, a decrease of up to 1.8% regarding the isobaric heat capacity was reported for the TiCN(1 wt.)/PG:W nanofluid. Furthermore, Newtonian behaviour of the samples was also observed, with an increase in dynamic viscosity of 6.7% for the highest concentrated dispersion.

**Keywords:** Titanium carbonitride, PG:W, thermal conductivity, isobaric heat capacity, dynamic viscosity.

## 1. Introduction

Due to the issues derived from the consumption of fossil fuels in the world, the optimization of the use of energy in industrial processes becomes very important. For several decades, efforts have been given to achieve a noticeable improvement in the heat transfer processes. To do this, it has been tried to reduce the size of the heat exchangers or the heat transfer time. Some conventional fluids have low thermal conductivity that directly affects the performance of the heat exchangers. This constitutes a limiting factor to improve the energy efficiency of these devices. To improve its thermal performance, it is proposed to enhance the intrinsic properties of fluids by dispersing solid nanoparticles with high thermal conductivity. Since Choi introduced the term nanofluid in 1995 [1], every year there are more studies showing that nanofluids improve heat transfer compared to conventional fluids. Among other examples, it has been shown that the dispersion of nanoparticles improves thermal conductivity [2] and convective heat transfer coefficient [3, 4]. Furthermore, the rheological properties of heat transfer fluids play a very important role in the applications where nanofluids can be applied, particularly in flowing conditions [5]. In this work, the mixture of propylene glycol and water at 20:80 mass ratio has been studied before and after containing different concentrations of TiCN dispersed nanoparticles. Nanofluids were prepared by dispersing TiCN nanoparticles with an average size of ~40 nm at concentrations from 0.1 to 1.0 wt.% in a binary mixture of propylene glycol:water 20:80 wt.% (PG:W). In order to improve the temporal stability of designed dispersions, poly(styrenesulfonate) (PSS) was used in a PSS:TiCN mass ratio of 1:10 in all cases. Propylene glycol was purchased from Sigma-Aldrich (Inc. St. Louis, MO. USA), with a mass purity of 99.5%. Commercial TiCN nanoparticles were supplied by PlasmaChem GmbH (Berlin, Germany), and PSS with an average mass molecular weight ~70.000(g/mol) was also provided by Sigma-Aldrich (Inc. St. Louis, MO. USA). The dispersions were designed using the two-step method and an ultrasonication probe treatment was applied to improve the dispersibility. Firstly, an evaluation of the temporal stability of the designed nanofluids was developed. The evolution of the hydrodynamic size of the particles within the dispersion was analysed during 15 days by a Zetasizer Nano ZS (Malvern Instruments Inc., UK) at 298 K. Thermal conductivity,  $k$ , of the base fluid and dispersions were measured in the liquid phase at temperatures between 278 and 303 K with 5 K step by a transient hot wire method [6], using a KD2 Pro thermal property analyzer (Decagon Devices, Inc., Pullman, WA, USA). Isobaric heat capacity,  $c_p$ , was determined

for base fluid (PG:W) and nanofluids through the quasi-isothermal temperature-modulated differential scanning calorimetry method by a Q2000 calorimeter (TA Instruments, New Castle, DE, USA) in the temperature range from 283 to 333 K. The rheological study was developed by a Physica MCR 101 rotational rheometer (Anton Paar, Austria). A stainless-steel cone-plate geometry CP50–1 (diameter of 50 mm) was selected to carry out the measurements. In this study, the temporal stability analysis, and the experimental study of the thermal conductivity, isobaric heat capacity, and dynamic viscosity of the proposed nanofluids, are presented.

## 2. Results and Discussion

The temporal stability was evaluated within two dispersions of TiCN(0.1wt.)/PG:W (PSS:TiCN ratio 1:10) by observing the variation of the hydrodynamic size of dispersed nanoparticles over time. The two studied samples were a static dispersion, i.e. the sample remains without movement during the days of the experiments, and a shaken dispersion, i.e. the sample is subjected to mechanical agitation by using a vortex before every size measurement.

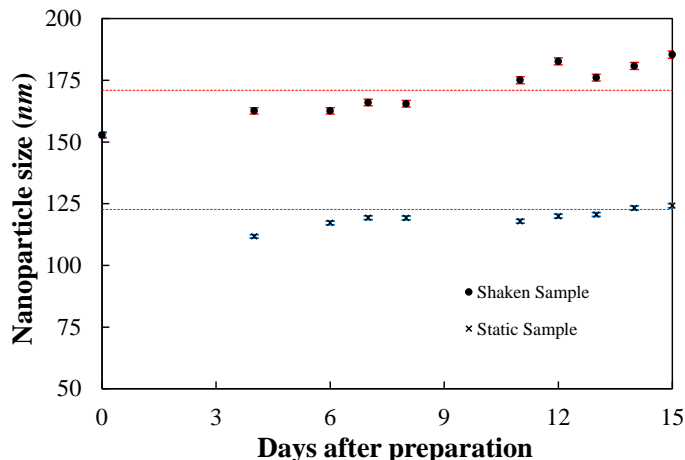


Figure 1: Temporal evolution of hydrodynamic size for the TiCN(0.1wt.)/PG:W (PSS:TiCN ratio 1:10) nanofluid.

Figure 1 shows as the hydrodynamic size of the nanoparticles in the static dispersion decreases during the first few days after preparation. This is because a small part of the nanoparticles might be slightly agglomerated and sedimented while the larger part the nanoparticles remain dispersed for a longer time. After these first days, the average zeta-size of the nanoparticles in the dispersion remains constant at around 123 nm. In addition, the shaken sample shows a slightly larger zeta-size than the original due to the agitation of those larger particles, with an average size around 171 nm, and it presents stable values throughout the days of measurements.

Figure 2 shows the temperature dependence of thermal conductivity for PG:W and different nanofluids, where the thermal conductivity remains practically unchanged for the lowest nanoparticle concentrations. It is observed that TiCN(1wt.)/PG:W showed a smaller increase in this property than the TiCN (0.5 wt%)/PG:W sample. This last sample showed the maximum increase in thermal conductivity of 4.7%.

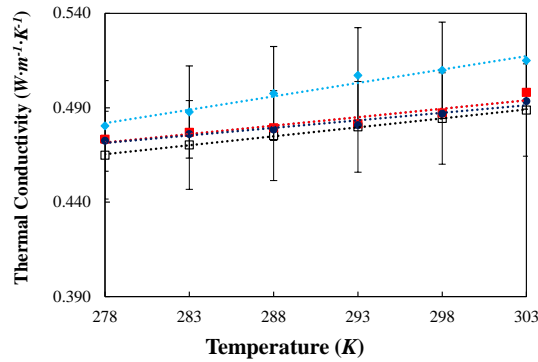


Figure 2: Temperature dependence of thermal conductivity for PG:W ( $\square$ ), TiCN(0.1wt.)/PG:W ( $\bullet$ ), TiCN(0.5wt.)/PG:W ( $\blacklozenge$ ), and TiCN(1wt.)/PG:W nanofluids ( $\blacksquare$ ). (.....) Linear fitting. Error bars indicate 5% uncertainty.

A similar behaviour was reported by Wang et al. [7] for nanofluids based on paraffin wax, where the thermal conductivity increased with the loading of  $\text{TiO}_2$  nanoparticles, but decreased from a concentration higher than 3 wt. %.

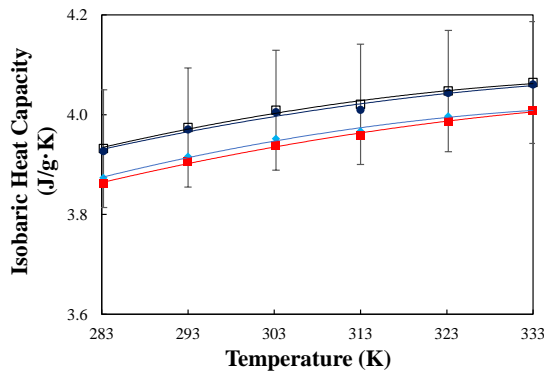


Figure 3: Temperature dependence of isobaric heat capacity of for PG:W ( $\square$ ), TiCN(0.1wt.)/PG:W ( $\bullet$ ), TiCN(0.5wt.)/PG:W ( $\blacklozenge$ ), and TiCN(1wt.)/PG:W nanofluids ( $\blacksquare$ ). (—) Second-order polynomial fitting. Error bars indicate 3% uncertainty [8].

Figure 3 shows the  $c_p$  decreasing with the concentration of TiCN nanoparticles. This decrease in  $c_p$  reaches 1.6% for the TiCN(1wt.)/PG:W nanofluid and 1.4% for the TiCN(0.5wt.)/PG:W nanofluid, and the differences between the base fluid and the nanofluid become smaller as the temperature increases.

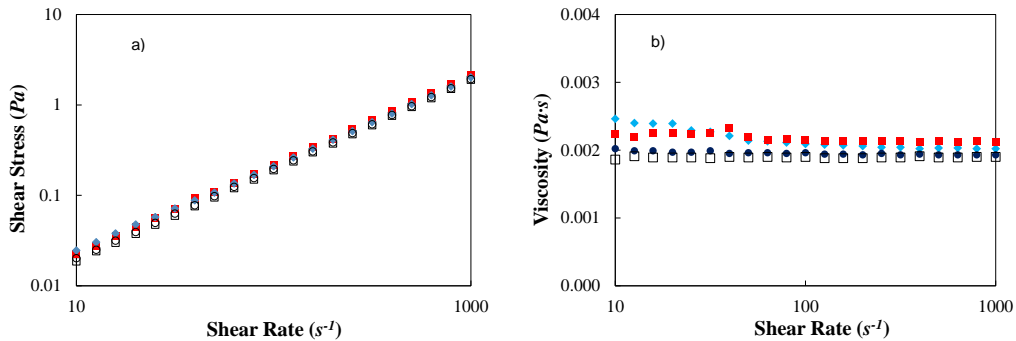


Figure 4: Shear stress as a function of shear rate (a) and dynamic viscosity (b) at 293 K for PG:W ( $\square$ ), TiCN(0.1wt.)/PG:W ( $\bullet$ ), TiCN(0.5wt.)/PG:W ( $\blacksquare$ ) and TiCN(1wt.)/PG:W nanofluids ( $\blacksquare$ ).

Figure 4a shows the relationship between shear stress and shear rate for the designed samples. As observed, the base fluid and nanofluids present Newtonian behavior under these conditions. In addition, Figure 4b shows the differences in viscosity at 303 K between the base fluid and two different nanofluids. The increase in the average viscosity value is 4.4% and 6.7% for TiCN(0.5wt.)/PG:W and TiCN(1wt.)/PG:W samples at 303 K,

### 3. Conclusions

The temporal stability, thermal conductivity, isobaric heat capacity, and dynamic viscosity of different TiCN concentrations dispersed in PG:W at 20:80 ratio have been analysed. TiCN shows ease of recovering the initial dispersibility with a simple mechanical agitation after 2 weeks, after adding PSS as a surfactant in a mass ratio PSS:TiCN 1:10. A thermal conductivity enhancement of 4.7%, an isobaric heat capacity reduction of 1.4%, and a dynamic viscosity increase of 4.4% are found for the TiCN(0.5%)/PG:W sample regarding the base fluid.

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### References

- [1] Choi, S.U., Eastman, J.A. Enhancing thermal conductivity of fluids with nanoparticles. Argonne National Lab.(ANL), Argonne, IL (United States), 1995.
- [2] Aguilar, T., Sani, E., Mercatelli, L., Carrillo-Berdugo, I., Torres, E., Navas, J. Exfoliated graphene oxide-based nanofluids with enhanced thermal and optical properties for solar collectors in concentrating solar power. *Journal of Molecular Liquids*. 2020, 306, 112862.
- [3] Murshed, S.M.S., Leong, K.C., Yang, C., Nguyen, N.T. Convective heat transfer characteristics of aqueous TiO<sub>2</sub> nanofluid under laminar flow conditions. *International Journal of Nanoscience*. 2008, 7, 325-31.
- [4] Ajeeb, W., Thieleke da Silva, R.R.S., Murshed, S.M.S. Experimental investigation of heat transfer performance of Al<sub>2</sub>O<sub>3</sub> nanofluids in a compact plate heat exchanger. *Applied Thermal Engineering*. 2023, 218, 119321.
- [5] Vallejo, J.P., Żyła, G., Fernández-Seara, J., Lugo, L. Influence of six carbon-based nanomaterials on the rheological properties of nanofluids. *Nanomaterials*. 2019, 9, 146.
- [6] Healy, J., De Groot, J., Kestin, J. The theory of the transient hot-wire method for measuring thermal conductivity. *Physica B+C*. 1976, 82, 392-408.
- [7] Wang, J., Xie, H., Guo, Z., Guan, L., Li, Y. Improved thermal properties of paraffin wax by the addition of TiO<sub>2</sub> nanoparticles. *Applied Thermal Engineering*. 2014, 73, 1541-7.
- [8] Cabaleiro, D., Colla, L., Agresti, F., Lugo, L., Fedele, L. Transport properties and heat transfer coefficients of ZnO/(ethylene glycol+ water) nanofluids. *International Journal of Heat and Mass Transfer*. 2015, 89, 433-43.