

Ethylene glycol based silver nanoparticles synthesized by polyol process: Characterization and thermophysical profile

Soukaina Zeroual, Patrice Estellé, David Cabaleiro, Brigitte Vigolo, Melanie Emo, Wafae Halim, Said Ouaskit

▶ To cite this version:

Soukaina Zeroual, Patrice Estellé, David Cabaleiro, Brigitte Vigolo, Melanie Emo, et al.. Ethylene glycol based silver nanoparticles synthesized by polyol process: Characterization and thermophysical profile. Journal of Molecular Liquids, 2020, 310, pp.113229. 10.1016/j.molliq.2020.113229. hal-02558309

HAL Id: hal-02558309 https://univ-rennes.hal.science/hal-02558309

Submitted on 29 Apr 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ethylene glycol based silver nanoparticles synthesized by polyol process: characterization and thermophysical profile

Soukaina Zeroual¹, Patrice Estellé^{2,*}, David Cabaleiro^{2,3}, Brigitte Vigolo⁴, Mélanie Emo⁴, Wafae Halim^{1,5}, Said Ouaskit¹

¹ Laboratoire de Physique de la matière Condensée, Faculté des SciencesBen M'Sik, University Hassan II of Casablanca, BP7955

² Univ Rennes, LGCGM, F–35000, Rennes, France

³ Departamento de Física Aplicada, Universidade de Vigo, E–36310, Vigo, Spain

⁴ Université de Lorraine, CNRS, Institut Jean Lamour UMR7198, F-54000 Nancy, France

⁵ Univ Le Mans, Department of Physics-Mechanics-Acoustics ,72085, le Mans, France

* Correspondence: patrice.estelle@univ-rennes1.fr; Tel.: +33(0)223234200

Abstract: This study reports the synthesis and the characterization of ethylene glycol silverbased nanofluids produced from the polyol process. This synthesis process is based on the reduction of silver nitrate (AgNO₃) with the presence of the aqueous emulsion of latex copolymer, used here for the first time along with ethylene glycol. The influence of latex copolymer content for a fixed amount of AgNO₃ for the production of silver-based nanofluids is investigated. The efficiency of the synthesis process is demonstrated from UV-Vis spectrometry, TEM and EDS characterization of the nanofluids. In addition, the dynamic viscosity of both the base fluids and nanofluids is experimentally measured over a wide shear rate and temperature range. While the base fluids behave in a non-Newtonian manner due to the presence of copolymer nanoparticles, it appears that the nanofluids are simply Newtonian without any noticeable viscosity enhancement compared to pure ethylene glycol. The thermal conductivity of the produced ethylene glycol silver-based nanofluids shows an enhancement of about 3% for the higher initial contents in copolymer latex. Such a thermophysical profile of ethylene glycol silver-based nanofluids is promising for their potential applications as circulating heat transfer fluids.

Keywords: Silver EG nanofluids; Latex copolymer; Nanoparticle characterizations; Dynamic viscosity; Thermal conductivity; Temperature effect

1. Introduction

The concept of nanofluids, based on the dispersion of nanoparticles with high intrinsic thermal properties within usual heat transfer fluids, was introduced in the early 1990s. Since

that time, nanofluids received growing attention due to their potential to be used particularly in heat transfer devices and energy systems because of their enhanced thermal conductivity. Among the common heat transfer fluids, ethylene glycol (EG) has been widely used to produce nanofluids [1,2]. A large variety of nanoparticle natures have been considered for ethylene-glycol nanofluid production such as for example MgO [3], TiN [4], BN [5], TiO₂ [6], ZnO [7] and carbon-based materials [8,9]. In all these works, an enhancement in thermal conductivity of the corresponding nanofluids was generally observed, this enhancement being dependent on nanoparticle content and temperature, as well as nanoparticle nature, shape, size, ... However, such an enhancement can be often accompanied by a rise in viscosity that can penalize the use of nanofluids in real heat transfer and cooling applications. It appears that silver nanoparticles are still weakly utilized to produce nanofluids, with EG as base fluid in particular, while silver possesses a high intrinsic thermal conductivity of about 420 W/mK [10], with also excellent optical and chemical properties, which make this material an excellent candidate as thermal conductivity enhancer. Microelectronics, energy supply, transportation, manufacturing or microchannels are some of the examples which have been identified as potential applications for advanced heat transfer media such as silver nanofluids [11-14].

The main previous studies about ethylene glycol silver (EGS) based-nanofluids are presented in the following. It can be noticed that EGS nanofluids are generally produced by one-step methods; silver nanoparticles being obtained from the reduction of silver nitrate (AgNO₃) with the help of reducing agents, stabilizers and capping agents. Nikkama and Toprak [11] prepared and investigated the transport properties of silver nanofluids based on water, ethylene glycol or an ethylene glycol-water mixture and containing nanoparticle mass loadings up to 2%. Authors observed that, in all three nanofluid sets, the enhancements in thermal conductivity were higher in value than the increases in dynamic viscosity, which may indict the potential of such nanostructured thermal fluids for several heat transfer applications. Polyacrylamide-co-acrylicacid (PAA-co-AA) was used in [13] for preparing EGS nanofluids and investigating the ratio of PAA-co-AA and AgNO₃. A thermal conductivity enhancement at ambient condition up to 14% for Ag weight fractions of only 10000 ppm was reported and good dispersion stability was noticed during two weeks despite the presence of aggregates. The effect of microwave heating and irradiation times on the properties of water and EG silver nanofluids was investigated in [15]. Here, the synthesis method was also assisted by polyvinylpyrrolidone (PVP) and the silver nanoparticles were formed during an irradiation process. This process mainly affects the distribution in silver nanoparticles rather than their size. EG appears as a good solvent and leads to better thermal diffusivity of nanofluids than water. The thermal properties of EGS nanofluids were also studied by Khamliche et al. [16] focusing on the shape effect of silver nanoparticles. Nanoparticles with high aspect ratio were obtained with EG and PVP as reducing agent that contributed to a larger enhancement in nanofluid thermal conductivity. The influence of the aspect ratio of the nanoparticles was also considered by Zhu et al. [17] who characterized EGS nanofluids where silver nanowires of different lengths were produced with PVP and FeCl₃.6H₂O. An enhancement in viscosity and thermal conductivity of the prepared nanofluids was revealed by these authors with a stronger effect of silver nanowires with larger length, 100 µm. In addition, Salehi et al. [18] produced water-based silver nanofluids using sodium borohydride and hydrazine as reducing agents and PVP as surfactant. These stable and non-agglomerated nanofluids were shown to possess higher thermal conductivity than water with an important role of PVP content in thermal behavior. The heat transfer and flow properties of EGS-based nanofluids were experimentally studied by Madhesh and Kalaiselvam [19]. In that paper, nanofluids were produced by the reduction of AgNO₃ with PVP and sodium borohydride as stabilizing and reducing agents. Then, the silver powder was dispersed in EG in the nanoparticle volume concentration 0.1-2 %. The thermal conductivity of nanofluids was shown to linearly increase with nanoparticle loading and temperature in the range 303-363 K. Recently, silver nanoparticles with small size were synthesized in ethanol by using latex copolymer as both reducing and stabilizing agent [20]. This study also reported the effect of precursor content and microwave irradiation power on the formation of silver nanoparticles that were stable for a long time in the solvent. Lastly, PVP-capped Ag nanoparticles, from 0.1 to 1.1 % in weight content and with an average size of 22 nm, were dispersed in poly(ethylene glycol) by Marcos et al. [21] for the synthesis of stable nanofluids. The presence of Ag nanoparticles was reported to improve the thermal conductivity and the sub-cooling property of poly(ethylene glycol) in particular for the higher content in Ag nanoparticles. The thermal conductivity of EG-nanofluids containing silver nanoparticles of different shapes (spherical, rod-shaped and plate-shaped nanoparticles) was also experimentally investigated by Fang et al. [14]. Larger improvements in thermal conductivity were reported in this last article for suspensions containing rod-shaped silver (in comparison to nanofluids prepared using similar concentrations of spherical or plate-shaped Ag nanoparticles), which authors attributed to the formation of a nanoparticle network that facilitates heat conduction. However, considerably higher increases in dynamic viscosity were observed for rod-shaped silver (when compared with spherical nanoparticles), which may become a penalty in thermal systems.

The heat transfer and flow performance of Ag/EG nanofluids, flowing through a tubular cooling heat exchanger, were experimentally studied by Madhesh and Kalaiselvam *et al.* [22]. Results revealed that, for the maximum nanoparticle concentration (2% in volume), convective heat transfer coefficient and pressure drop increased by 49% and 23.7%, respectively. On the other hand, the surface plasmon resonance of silver nanoparticles (with a high absorption peak near sunlight's peak irradiance) also makes this nanomaterial well-suited to improve the solar thermal conversion efficiency of conventional working fluids [23]. Several studies [23-25] investigated the potential of silver aqueous dispersions as solar absorber and heat transfer media in direct absorption solar thermal collectors.

In this study, the synthesis and the characterization of ethylene glycol silver-based nanofluids are reported. As done previously with ethanol [20], the synthesis process is based on the reduction of AgNO₃ (99%) with the presence of an aqueous emulsion of latex copolymer namely vinyl-acetate/vinyl-versatate. This copolymer latex is here used for the first time with EG. The presence and characterization of silver nanoparticles is evaluated from UV-Vis spectra, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analysis showing the efficiency of the synthesis process in EGS-based nanofluids. Finally, the dynamic viscosity and thermal conductivity of these nanofluids are experimentally obtained. Such a study is performed considering the influence of the latex copolymer content on the formation of silver nanoparticles and the effect on the thermophysical properties of the developed nanofluids as potential efficient thermal fluids.

2. Materials and methods

2.1 Materials

For the synthesis and the production of EGS-based nanofluids, the following materials were used as received. The silver nitrate (AgNO₃, 99.9 % purity without any further purification) was used as a precursor of Ag [20]. Ethylene glycol (Acros Organics, CAS 107-21-1, New Jersey, USA; density of 1.1130 g/cm³ and 98 % purity) was used as a solvent. An aqueous emulsion of latex copolymer, prepared by the Maghrebian Polymers Society [20], was used as

reducing and capping agent. The influence of latex copolymer (acetate versatate) content for production, dispersion and stability of silver nanoparticles was considered in this study.

2.2 Nanofluid preparation

The silver nanoparticles were synthesized by the polyol method known as a one-step chemical method involving the simultaneous production and dispersion of the nanoparticles into the base fluid. This method is simple, fast and inexpensive and it can be used for the synthesis of different metallic nanoparticles. In the present study, the EGS-based nanofluids have been prepared by the reduction of AgNO₃ in the presence of latex copolymer within EG. For preparing the nanofluids the following procedure has been established. First, 20 mL of EG is mixed with the latex copolymer in a clean glass container using an ultrasonic bath (Transonic, TI-H-5, Fisher Bioblock Scientific, Illkirch-Graffenstaden, France) for 10 min at a frequency of 130 kHz. Four different contents of copolymer were considered, *viz.* 99, 126, 305 and 340 mg. Thereafter, a fixed amount of AgNO₃ (21 mg) was added to each solution then placed under magnetic and thermal stirring. The heating setup used for the preparation of silver nanofluids consisted in a hotplate magnetic stirrer (RCT Basic IKA Werke). Each sample was heated up to 120 °C and reacted for 35 min until the initial colorless solution changed from faint yellow to golden yellow color.

2.3 Characterization techniques

UV–Vis spectrophotometry analysis was used to characterize the optical properties of the prepared nanofluids and to evidence the formation of silver nanoparticles. The standard UV-Visible analysis was performed with an UV 3100 Selecta Spectrophotometer (J.P. Selecta S.A., Abrera, Spain) in the spectra range from 300 to 600 nm using a quartz cuvette. Before each measurement of nanofluids, the corresponding base fluid composed of ethylene glycol and latex was used as reference to take the blank solution.

Also, scanning electron microscopy (SEM) characterization of EG and both base fluids and nanofluids was performed with a JEOL-JSM-7100F (JEOL USA Inc., Peabody, USA) equipment coupled with energy dissipative X-ray spectrometer (EDS) to evaluate, at first sight the reliability of the synthesis process. The samples were prepared by depositing a drop on a carbon substrate and then dried at ambient conditions before SEM characterization.

Nanofluid samples were diluted in ethanol before being deposited on a copper grid covered by an amorphous carbon film for TEM / Scanning TEM (STEM) experiments. TEM / STEM

investigations were performed using a JEOL ARM 200 F (JEOL Ltd., Tokyo, Japan) equipped with a Cold Field Emission Gun (FEG) operating at 200 kV and a spherical aberration (Cs) probe corrector. Both bright field (BF) and high-angle annular dark field (HAADF) modes were used for the observations. Chemical compositions were determined using EDS. The EDS spectra were recorded on a JEOL spectrometer (SDD). Around 30 images were collected for each sample to ensure a good representative analysis of the samples. The Image J software was used for the particle size analysis.

The rheological properties and the dynamic viscosity of both base fluids and nanofluids were evaluated by a stress-controlled rheometer Malvern Kinexus Pro (Malvern Instruments, Ltd, Worcestershire, UK) under controlled temperature and with a cone and plate geometry of 60 mm in diameter and 1° in angle. The temperature of the system was controlled by a unit placed below the lower plate that allowed regulating the temperature by Peltier effect. The volume of the sample was taken with a syringe-type automatic pipette then set up to the lower plate, stand at attention that no air bubbles were formed in the sample. The excess of sample was removed after the displacement of the cone to reach the required sample gap of 0.03 mm. Then, each sample was left to rest for 5 min at the required temperature. Each measurement was reiterated at least twice to check the stability and the repeatability of the results. The measurements were performed as a function of temperature from 20 to 50°C, with an interval of 10 °C, and data were collected under steady-state conditions applying a shear stress ramp to cover a shear rate range between 10-1000 s⁻¹. The cone and plate were carefully cleaned with acetone after each measurement. EG was also measured to evaluate the uncertainty in viscosity determinations and the possible viscosity enhancement of nanofluids, as described further in Results and Discussion section.

The thermal conductivity of the base fluids and nanofluids was measured in the temperature range 20-50°C with a THW-L2 device (Thermtest Inc., Canada) based on the transient short hot-wire technique following the ASTM D7896 standard. Such a device is appropriated to measure liquid thermal conductivity from 0.01 to 2 W/mK and in the temperature range between -10 and +100 °C with a small quantity of sample of about 20 mL. Testing probe consists of a wire (made of Alumel, with a length of 60 mm and a diameter of 1 mm) and incorporates a temperature sensor (\pm 0.1 °C). For performing measurements, a sample holder was first filled with the tested sample in which the probe was vertically immersed. Such holder was then placed within a dry bath. After the achievement and stabilization at the required temperature, the measurement started by applying a power supply of 140 mW to the

wire with a test time of 1.5 s avoiding convection. The thermal conductivity was evaluated from the slope of the temperature rise versus the time logarithm in the linear region using the THW-L2 software. Previously, both the probe temperature sensor and hot wire sensor have been carefully calibrated with distilled water (DIUF, CAS 1132-18-5, Fisher Chemical, 0.599 W/mK) at 20 °C. Acetone and distilled water were also used to clean the probe and the container between each sample measurement. Each reported value consisted in an average of at least five measurements. The thermal conductivity of EG was measured and compared to the literature to assess the reliability and uncertainty of the measurements, as described later in Section 3.2.

3. Results and Discussion

3.1 Characterizations of nanofluids

First, a sign for the formation of silver nanoparticles within the base fluids could be observed by a visual color change of the solutions from colorless before the reaction to faint yellow and finally golden yellow after the synthesis. Figure 1 shows that the obtained nanofluids, their color depends, as expected, on the latex copolymer content: higher content in copolymer leads in higher silver nanoparticle concentration within the suspensions. This visual observation is also confirmed by UV-Vis measurements as shown in Figure 2. A surface plasmon surface (SPR) band at 350-500 nm with a broad peak entered at about 400-450 nm can be noticed for all the EGS-based nanofluids. This SPR was created by surface plasmon vibrations in the silver nanoparticles, revealing that way their presence within the samples. Moreover, the absorption spectra exhibit a dependence on latex concentration. The absorbance of the localized SPR band is more pronounced as the concentration of copolymer latex increases from 99 to 340 mg. Such enhancement could be due to an increase in yield of the synthesized silver nanoparticles as the copolymer latex content is increased. The position of SPR may also be correlated to the mean size and the size distribution of the metal nanoparticles. When the SPR bands become sharper, this corresponds to the existence of small size and narrow distribution of the Ag nanoparticles. For the studied samples, sharper SPR is observed for the lowest copolymer concentration meaning that the highest copolymer concentrations induce larger Ag nanoparticles with a broader distribution size meaning that the copolymer favors the nanoparticle formation.



Figure 1: Photographs of the EGS-based nanofluids after Ag/EG synthesis prepared with different content of copolymer latex: (1) 99 mg, (2) 126 mg, (3) 305 mg, (4) 340 mg of copolymer latex, respectively.



Figure 2. UV-Vis spectra of EGS-based nanofluids for different initial copolymer latex concentration: 99 mg (open black triangle), 126 mg (open red circle), 304 mg (open dark blue square), 340 mg (open pink diamond) of copolymer latex, respectively.

SEM images of both the base fluids (EG and copolymer) and the nanofluids prepared with different copolymer content are reported in Figure 3. On the left side images (Figs. 3a, 3c, 3e and 3g), for all the samples, one can observe two different shapes: a spherical shape attributed to the copolymer latex particles and flower-like structure. It should be mentioned that the

flower-like structure appearing is attributed to EG, as confirmed by SEM observations of EG alone (not reported here). As expected, the number of the copolymer latex particles increases (with respect to the EG particles) with the initial content in copolymer. In addition, after the synthesis of the silver nanoparticles (Figs. 3b, 3d, 3f and 3h), a significant part of the copolymer latex is no more present on the SEM images. It has probably been consumed by the synthesis reaction. Particles, mainly in form of aggregates, are visible on the SEM images of nanofluids, and consist in capped Ag nanoparticles, as identified by EDS.



Figure 3: SEM images of base fluids (EG and copolymer latex) (a, c, d, g) and the EGS nanofluids (b, d, f, h) for different copolymer latex content: (a and b) 90 mg, (b and c) 126 mg, (d and f) 305 mg and (g and h) 340 mg.

The silver-based particle size was investigated by TEM analysis. Compared to SEM, TEM allowed directly visualizing the particles since it was possible to differentiate between the most electronically dense silver particles and the polymer. In BF images, the polymer appears as light grey zone and the silver particles are the dark more or less spherical particles, as shown in figure 4 and figures 5a. The difference in light grey zones in the images of the figures 4a (well visible grey zones) and 4c (grey zone not visible) can be related to the difference in copolymer content for these two samples. Moreover, for the sample prepared with 99 mg of copolymer, the Ag nanoparticles are well dispersed on the TEM grid contrary to the sample prepared with 340 mg of copolymer for which the Ag particles are agglomerated together with the polymer. The HAADF observations allows to well reveal the presence of the polymer around the silver particles but also out of the silver particle zones (shown by the arrows in Figure 5b). EDS spectra of same samples are shown in Figure 6 confirming the presence of silver nanoparticles without the presence of visible impurities.

Due to the presence of large particles that represent a significant part of the images, it was difficult to estimate with eyes only their mean size or their distribution in size, this is the reason why the Image J software was used for the size analysis of the silver nanoparticles. The results reveal that most of particles have a diameter lower than 8 nm with mean diameter around 2-3 nm (Figure 7). The shape of these low-size particles is rather spherical while the larger particles (whose diameter can reach several tens of nm) can have spherical, elongated or distorted shapes, as shown in Figures 4 and 5.



Figure 4. TEM micrographs of EGS-based nanofluids synthesized with 340 (a and b) and 99 mg of copolymer (c and d), respectively at different magnifications.



Figure 5. STEM micrographs in BF (a) and HAADF modes (b) of the sample at initial concentration of 340 mg of copolymer, the same zone is observed for the two imaging modes.



Figure 6. EDS spectra focused on the nanoparticles from the samples prepared at two different initial copolymer concentrations, 340 mg (a) and 90 mg (b), respectively.



Figure 7. Size distribution of the silver particles analyzed from TEM images of a sample with an initial copolymer content of 340 mg by means of Image J.

3.2 Thermophysical properties of nanofluids

3.2.1 Rheological properties and dynamic viscosity

First, the shear flow curves of EG in the temperature range 20-50°C are reported in Figure 8a. As expected for pure EG, a Newtonian behavior is observed for each temperature, as the dynamic viscosity is constant within the shear rate range studied. Also, the viscosity exhibits the general inherent downward trend with increasing temperature, as shown in Figure 8b. An absolute average deviation (AAD) of 3 % was obtained in the temperature range 20-50°C in comparison to the results of Yang *et al.* [26].



Figure 8. Dynamic viscosity of EG in function of shear rate (a) and temperature (b)

The shear flow curves of base fluids (EG and copolymer latex) and the EGS-based nanofluids at 40 °C are reported in Figure 9. Contrary to what was observed for EG alone (Figure 8a), the mixtures of EG and copolymer latex used as base fluids behave as shear-thinning materials as the dynamic viscosity decreases with shear rate. This can be explained by the interactions between the molecules of copolymer latex and EG. Thus, higher the content in copolymer latex, stronger the copolymer-EG interactions. The shear-thinning effect is thus much more pronounced over a larger shear-thinning region as the concentration of copolymer latex is increased in the samples. Remarkably, it is observed in the same figure that the nanofluids behave in Newtonian manner with no noticeable difference between each nanofluid within the experimental uncertainty and without any significant modification in viscosity regarding pure EG. The copolymer latex which has been largely consumed by the synthesis of silver nanoparticles (in agreement with SEM/TEM characterizations) and so it cannot induce any intrinsic effect in rheology behavior of the EGS-based nanofluids. Then, the presence of silver nanoparticles does not significantly modify the viscosity of the EGS-based nanofluids compared to that of the EG alone. This is of practical interest in view of possible applications as pressure drop and pumping power of energy systems involving nanofluid flow strongly depend on viscosity.



Figure 9. Dynamic viscosity versus shear rate for base fluids and nanofluids at a temperature of 40 $^{\circ}$ C.

Similar trends in dynamic viscosity were observed for the EGS-based nanofluids for other tested temperatures (20, 30 and 50 °C) All shear flow curves of the EGS-based nanofluids are gathered in Figure 10(a) together with the behavior at 40 °C. A Newtonian feature is as well here evidenced for all the nanofluids in the 20-50°C temperature range. In addition, the viscosity values of the prepared EGS-based nanofluids are also plotted in Figure 10(b). As expected, an increase in temperature of the nanofluids leads to a decrease of their viscosity. Again here, the presence of the silver nanoparticles only slightly impacts the viscosity of these EGS-based nanofluids. One can notice the quasi-overlapping of the viscosity values of pure EG and the nanofluids in the figure 10b. In the studied temperature range, the difference between pure EG and nanofluid viscosity is lower than the experimental uncertainty.



Figure 10. Dynamic viscosity versus shear rate for all nanofluids in the temperature range 20- 50° C (a) - Dynamic viscosity of nanofluids in comparison to pure EG (b).

3.2.2 Thermal conductivity

The thermal conductivity values of pure EG are reported in Figure 11(a) and compared to literature data. It is shown that these values are in quite good agreement with the data of [27] and the data of [5], with AADs of 0.04 % and 0.48 %, respectively, in the temperature range

20-50°C. This allows the experimental procedure to be validated and used with base fluids and nanofluids. Note that the error bars represent the standard deviation between measurements.

Figure 11(b) shows the thermal conductivity of EG and copolymer latex base fluids with the lowest and highest content of copolymer latex used. The presence of copolymer latex does not significantly modify the thermal conductivity of pure EG. Consequently, the observed thermal conductivity increase of the EGS-based nanofluids is only attributed to the presence of silver nanoparticles.

The thermal conductivity of the EGS-based nanofluids with different initial contents of copolymer latex and temperature is reported in figures 12 (a) and (b). For the lower contents in copolymer latex (99 and 126 mg), figure 12(a) evidences that the thermal conductivity of EGS-based nanofluids produced is similar to that of pure EG. So, when silver nanoparticles were produced with these two low quantities of copolymer latex, as previously shown in section 3.1, the silver nanoparticle content was not high enough to induce an enhancement in thermal conductivity of EG. On the contrary, when the nanofluids were produced with higher initial contents in copolymer latex (304 and 340 mg,), the thermal conductivity of the nanofluids is significantly higher than that of pure EG (Figure 12(b)). This enhancement is attributed to the higher number of silver nanoparticles produced with a higher amount copolymer latex (in agreement with visual observations and UV-Vis spectra, figures 1 and 2). For an amount in copolymer latex higher than ~ 300 mg, the content of silver nanoparticles is high enough to induce a thermal conductivity enhancement. This enhancement seems to reach an optimum with the content of precursor initially considered since it is not further modify as higher copolymer latex was used. The temperature dependence of thermal conductivity is similar for both EGS-based nanofluids, and it is also similar to the temperature tendency of pure EG. An average enhancement between 2.5 and 3% is noticed for all temperatures in comparison to EG. Such a result, combined with the unmodified viscosity value, is of interest with regards of the possible use of these nanofluids in real energy systems. This order of magnitude in thermal conductivity enhancement of SEG nanofluids was also reported earlier in [11,28] for example, for known and higher content in silver nanoparticles.



Figure 11. Thermal conductivity of pure EG with (a) comparison of literature data and (b) EG mixed with copolymer latex.



Figure 12. Comparison of thermal conductivity of pure EG with (a) EGS-based nanofluids produced with the two lowest contents in copolymer latex and (b) nanofluids produced with the two highest contents in copolymer latex.

4. Conclusions

This study reports the synthesis and the characterization of EGS-based nanofluids. The synthesis process was based on the reduction of AgNO₃ with the presence of an aqueous emulsion of copolymer latex namely vinyl-acetate/vinyl-versatate. The presence and characterization of the silver nanoparticles were investigated by UV-Vis spectra, TEM, STEM and EDS analyses. The results have shown the efficiency of the synthesis process for EGS-based nanofluid development. Characterization by TEM revealed the non-agglomeration of the silver nanoparticles after their preparation probably thank to the presence of copolymer latex. Interestingly, the synthesis approach allowed an efficient synthesis of silver nanoparticles which re-aggregation was limited, producing good stability nanofluids.

In addition, these EGS-based nanofluids behaved as Newtonian fluids without any significant enhancement in dynamic viscosity in comparison to pure EG in the 20-50 °C range. Finally, it was observed that the thermal conductivity of EGS-based nanofluids was enhanced by 3 % in comparison with EG for the two highest used contents in copolymer latex in the same temperature range. Such a result is of interest and promising in terms of application as the dynamic viscosity was still remained unchanged. Future works could consist in adjusting the content in copolymer latex and Ag precursor to increase further the thermal conductivity without modifying the dynamic viscosity.

References

[1] S.M. Sohel Murshed, C.A. Nieto de Castro, Conduction and convection heat transfer characteristics of ethylene glycol based nanofluids – A review, Applied Energy, 184 (2016) 681-695.

[2] G. Sekrani, S. Poncet, Ethylene and propylene glycol based nanofluids: A literature review on their thermophysical properties and thermal performances, Applied Sciences 8 (11) (2018) 2311.

[3] G. Żyła, Viscosity and thermal conductivity of MgO–EG nanofluids, Journal of Thermal Analysis and Calorimetry 129 (1) (2017) 171-180.

[4] G. Żyła, J. Fal, P. Estellé, Thermophysical and dielectric profiles of ethylene glycol based titanium nitride (TiN–EG) nanofluids with various size of particles, International Journal of Heat and Mass Transfer 113 (2017) 1189-1199.

[5] G. Żyła, J. Fal, J. Traciak, M. Gizowska, K. Perkowski, Huge thermal conductivity enhancement in boron nitride–ethylene glycol nanofluids, Materials Chemistry and Physics 180 (2016) 250-255.

[6] D. Cabaleiro, M.J. Pastoriza-Gallego, C. Gracia-Fernández, M.M. Piñeiro, L. Lugo, Rheological and volumetric properties of TiO₂-ethylene glycol nanofluids, Nanoscale research letters 8 (2013) 286.

[7] D. Cabaleiro, L. Colla, F. Agresti, L. Lugo, L. Fedele, Transport properties and heat transfer coefficients of ZnO/(ethylene glycol+ water) nanofluids, International Journal of Heat and Mass Transfer 89 (2015) 433-443.

[8] M. Shamaeil, M. Firouzi, A. Fakhar, The effects of temperature and volume fraction on the thermal conductivity of functionalized DWCNTs/ethylene glycol nanofluid: An experimental study, Journal of Thermal Analysis and Calorimetry, 126(3) (2016) 1455–1462.

[9] G. Żyła, J. Fal, P. Estellé, The influence of ash content on thermophysical properties of ethylene glycol based graphite/diamonds mixture nanofluids, Diamond and Related Materials 74 (2017) 81-89.

[10] A. H. Pordanjani, S. Aghakhani, M. Afrand, B. Mahmoudi, O. Mahian, S. Wongwises, An updated review on application of nanofluids in heat exchangers for saving energy, Energy Conversion and Management, 198 (2019) 111886.

[11] N. Nikkam, M.S. Toprak, Fabrication and thermo-physical characterization of silver nanofluids: An experimental investigation on the effect of base liquid, International Communications in Heat & Mass Transfer, 91 (2018) 196-200.

[12] E. Şimşek, S. Coskun, T. Okutucu-Özyurt, H. E. Unalan, Heat transfer enhancement by silver nanowire suspensions in microchannel heat sinks, International Journal Thermal Science, 123 (2018) 1-13.

[13] P. Sharma, I-H. Baek, T. Cho, S. Park, K. B. Lee, Enhancement of thermal conductivity of ethylene glycol based silver nanofluids, Powder Technology, 208(1) (2011) 7-19.

[14] X. Fang, Q. Ding, L-W. Fan, Z-T. Yu, X. Xu, G-H. Cheng, Y-C. Hu, K-F Cen, Thermal conductivity enhancement of ethylene glycol-based suspensions in the presence of silver nanoparticles of various shapes, Journal of Heat Transfer, 136 (2014) 034501.

[15] M. Noroozi, S. Radiman, A. Zakaria, S. Soltaninejad, Fabrication, characterization and thermal property evaluation of silver nanofluids, Nanoscale Research Letters, 9 (2014) 645.

[16] T. Khamliche, S. Khamlich, T.B. Doyle, D. Makinde, M. Maaza, Thermal conductivity enhancement of nano-silver particles dispersed in ethylene glycol based nanofluids, Materials Research Express, 5(3) (2018) 035020.

[17] D. Zhu, G. Huang, L. Zhang, Y. He, H. Xie, W. Yu, Silver nanowires contained nanofluids with enhanced optical absorption and thermal transportation properties, Energy and Environmental Materials, 2 (2019) 22-29.

[18] J.M. Salehi, M.M. Heyhat, A. Rajabpour, Enhancement of thermal conductivity of silver nanofluid synthesized by a one-step method with the effect of polyvinylpyrrolidone on thermal behaviour, Applied Physics Letters, 102 (2013) 231907.

[19] D. Madhesh, S. Kalaiselvam, Experimental study on the heat transfer and flow properties of Ag-ethylene glycol nanofluid as coolant, Heat Mass Transfer, 50 (2014) 1597-1607.

[20] M. Ider, K. Abderrafi, A. Eddahbi, S. Ouaskit, A. Kassiba, Silver metallic nanoparticles with surface plasmon resonance: Synthesis and applications, Journal of Cluster Science, 28 (2017) 1051.

[21] M. A. Marcos, D. Cabaleiro, S. Hamze, L. Fedele, S. Bobbo, P. Estellé, L. Lugo, NePCM based on silver dispersions in poly(ethylene glycol) as a stable solution for thermal storage, Nanomaterials 10 (2020) 19.

[22] D. Madhesh, S. Kalaiselvam Experimental study on the heat transfer and flow properties of Ag–ethylene glycol nanofluid as a coolant, Heat Mass Transfer, 50 (2014) 1597–1607.

[23] M. Chen, Y. He, J. Zhu, Y. Shuai, B. Jiang, Y. Huang, An experimental investigation on sunlight absorption characteristics of silver nanofluids, Solar Energy, 115 (2015) 85-94.

[24] E. Sani, P. Ninni, L. Di Colla, S. Barison, F. Agresti, Optical properties of mixed nanofluids containing carbon nanohorns and silver nanoparticles for solar energy applications, Journal of Nanoscience and Nanotechnology, 15(5) (2015) 3568-3573.

[25] T. B. Gorji, A.A. Ranjbar, A review on optical properties and application of nanofluids in direct absorption solar collectors (DASCs), Renewable and Sustainable Energy Reviews, 72 (2017) 10-32.

[26] C. Yang, P. Ma, F. Jing, D. Tang, Excess Molar Volumes, Viscosities, and Heat capacities for the mixtures of ethylene glycol + water from 273.15 K to 353.15 K, Journal of Chemical & Engineering Data, 48 (2003) 836-840.

[27] M. J. Pastoriza-Gallego, L. Lugo, J. L. Legido, M. M. Piñeiro, Thermal conductivity and viscosity measurements of ethylene glycol-based Al₂O₃ nanofluids, Nanoscale Research Letters, 6, (2011) 221.

[28] L. Zhang, W. Yu, D. Zhu, H. Xie, G. Huang, Enhanced thermal conductivity for nanofluids containing silver nanowires with different shapes, Journal of Nanomaterials (2017) 5802016.

Aknowledgements: P.E. acknowledges the European Union through the European Regional Development Fund (ERDF), the Ministry of Higher Education and Research, the French region of Brittany and Rennes Métropole for the financial support related to the device used in this study for thermal conductivity measurements. D.C. is recipient of a postdoctoral

fellowship from Xunta de Galicia (Spain). Authors acknowledge Francis Gouttefangeas from CMEBA (Université Rennes 1) for performing SEM studies. B. Vigolo and M. Emo thanks the Competence Center 3M at the Institute Jean Lamour and they are grateful to Dr. J. Ghanbaja for his valuable help for TEM investigation.

Conflicts of Interest: The authors declare no conflict of interest.