Research paper

Characterization of halloysite-water nanofluid for heat transfer applications

J.A. Alberola [a], R. Mondragón [b], J.E. Juliá [b], L. Hernández [b], L. Cabedo [a,*]

[a] Polymers and Advanced Materials Group (PIMA), Universitat Jaume I, Campus de Riu Sec, 12071 Castellón de la Plana, Spain
[b] Departamento de Ingeniería Mecánica y Construcción, Universitat Jaume I, Campus de Riu Sec, 12071 Castellón de la Plana, Spain

A B S T R A C T

Nanofluids based on water with halloysite (Hal) nanotubes were prepared and characterized in order to evaluate its suitability to be used as a heat transfer fluid. A characterization of the Hal powder nanoparticles was performed by means of SEM, TEM, WAXS, FTIR and TGA so that chemical composition, size and shape were determined. Stability of nanofluids was analyzed by means of zeta potential and light transmission measurements. Thermal conductivity, specific heat and viscosity of nanofluids prepared at different solid contents (0.5, 1, 3 and 5% volume fraction) and temperatures (40, 60 and 80 °C) were obtained in order to optimize the Prandtl number. The nanofluids exhibited a good performance for its application as heat transfer fluids, with low Prandtl numbers compared to other commonly used nanofluids. High thermal conductivity enhancement with moderate viscosity and good stability results was obtained for the Hal nanofluid.

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1. Introduction

A technological approach to reduce energy consumption is to enhance performance of heat exchange systems. Heat transfer plays an important role in many fields such as power generation, chemical processes, air conditioning, transportation, microelectronics and any application in which heating and cooling processes are involved. The enhanced efficiency would allow reducing the size of the devices and decrease the operating costs of associated processes (Fan and Wang, 2011; Godson et al., 2010; Özerinç et al., 2010).

One of the parameters limiting the performance of heat exchange systems is the inherent low thermal conductivity of conventional heat transfer fluids. In the last years intensive research efforts have increased to solve this problem. As possible alternative could be the addition of solid particles with thermal conductivity higher than that of the fluid. In 19th century, Maxwell first dispersed small particles into a base fluid (Maxwell, 1873). Further works demonstrated that the addition of micrometer- or millimeter-sized particles enhances heat transfer properties but it causes sedimentation of large particles, clogging of flow channels, erosion of pipelines and pressure drops. This problem can be solved by adding nanoparticles (colloidal particles with main size smaller than 100 nm) into the base fluid. High specific surface of nanoparticles, high dispersion stability, reduced particle clogging and adjustable properties make nanofluids an interesting solution to

enhance the performance of heat exchange systems (Buongiorno et al., 2009; Li et al., 2009; Özerinç et al., 2010; Saidur et al., 2011).

Due to advances in nanotechnology, Masuda et al. (1993) first dispersed alumina (Al_2O_3) ultrafine particles (13 nm in the mean diameter) in water, increasing thermal conductivity by 30%. Choi (1995) proposed the concept of nanofluid (dilute dispersions with solid particles smaller than 100 nm) to enhance thermal conductivity. Lee et al. (1999) dispersed alumina and copper oxide (CuO) nanoparticles in water and ethylene glycol (EG). These authors found that thermal conductivity increased linearly with the volume fraction. Nanofluid attention grew when Eastman et al. (2001) reported their results in nanofluids with copper (Cu) nanoparticles and EG as base fluid. They found a substantial enhancement of thermal conductivity. The same year Choi et al. (2001) dispersed multiwall carbon nanotubes (MWCNT) in water measuring an enhancement up to 160% at only 1% volume fraction of MWCNT. From this moment, there have been many studies in three kinds of nanoparticles dispersed in heat transfer fluids, namely metallic particles as aluminum (Al) (Murshed et al., 2008) and gold (Au) (Putnam et al., 2006), CNT (Biercuk et al., 2002; Segarra et al., 2013; Xie et al., 2003), and non-metallic particles as silica (SiO_2), alumina (Al_2O_3) (Mondragon et al., 2013) and titania (TiO_2) (Murshed et al., 2005). The convective heat transfer coefficient has been also studied (Juliá et al., 2012; Kim et al., 2009a,b).

However, different results and trends were found for the same materials characterized by different researchers, depending mainly in the procedure followed to prepare the nanofluids and the final state of agglomeration of the solid particles. In order to compare the values of thermal conductivity obtained by different researchers, a benchmark

* Corresponding author. Tel.: +34 964728193.
  E-mail address: lcabedo@uji.es (L. Cabedo).

study was carried out (Buongiorno et al., 2009). The same samples of Al_2O_3, SiO_2, Au and Mn–Zn ferrite nanofluids were analyzed by several laboratories, at room temperature (ranging from 20 to 30 °C), using the different available techniques, so the results could be compared and experimental error could be determined.

The lack of agreement between experimental results and theory has inspired efforts in identifying responsible heat transfer mechanisms (Fan and Wang, 2011): (1) liquid-layering, (2) aggregation, (3) particle motion, and (4) others. The second mechanism stimulates phonons transference along large particles or particle aggregates, which involves that particles with large aspect ratio have better heat transfer properties (Fan and Wang, 2011; Ghosh et al., 2013; Özerinç et al., 2010). As a result, the size and shape of nanoparticles and clusters formed are the key factors for the thermal conductivity enhancement (Gao et al., 2009; Prasher et al., 2006; Shima et al., 2010; Warrier et al., 2010; Wu et al., 2010). It was demonstrated that chain-like structures and nanotubes or nanofibers provide the highest thermal conductivity. Because of this, researches have focused on the use of carbon nanotubes to enhance thermal properties of fluids (Ding et al., 2006; Garg et al., 2009; Kim et al., 2009a,b; Talaei et al., 2011).

Although the addition of nanoparticles improves the thermal properties and heat transfer capabilities of fluids, the industrial applicability of nanofluids in heat transfer systems is limited by the increase of the viscosity of the fluid (which increases the pumping power). However, as also occurred with the conductivity measurement, the viscosity of nanofluids is highly dependent on the degree of agglomeration of the particles so that very different results can be obtained depending on the particle size and shape, being the chain-like structures those presenting the highest viscosities. Therefore, the use of carbon nanotubes is limited by its high viscosity. Hence, the combined study of thermal properties (thermal conductivity and specific heat) and rheological properties (viscosity) is of great importance, although only few works include rheological measurements of nanofluids (Lee et al., 2008; Pastoriza-Gallego et al., 2009, 2011; Yu et al., 2012). As it was done for thermal conductivity, a benchmark study was carried out (Venerus et al., 2010), in order to compare the values of viscosity obtained by different researchers, when the same samples of Al_2O_3, SiO_2, and Mn–Zn ferrite nanofluids were analyzed by several laboratories, at room temperature (ranging from 20 to 26 °C).

One of the challenges in thermal applications is to find a nanofluid providing the best thermal conductivity to viscosity ratio thus increasing the efficiency of heat transfer processes. Recently, thanks to its structure and properties, halloysite (Hal) nanotubes have increased their interest for the nanotechnology of advanced materials in areas such as catalysis, drug delivery, biomedical implants, corrosion protection of metals, biosensors, organic synthesis, flame retardant coatings, specific ion adsorbents, materials for sustained release of herbicides and antimicrobials and energy storage devices (Deen et al., 2012). Hal is a clay mineral of the kaolin group, having a hollow tubular-like structure with particle sizes within the nanometrical size range and large aspect ratio. The outer diameter of typical Hal nanotubes is within the range of 15–100 nm, and length is between 500 and 1500 nm (Alhuthali and Low, 2013; Cavallaro et al., 2012; Lvov et al., 2008; Pasbakhsh et al., 2013; Vergaro et al., 2010). The size and shape of Hal nanotubes together with its chemical composition and structure make this material a good candidate to be dispersed in water, thus obtaining an interesting nanofluid for heat transfer applications. Other interesting applications of Hal nanotubes are as carriers for drug delivery, adsorbents and fillers in clay polymer nanocomposites (Tan et al., 2014)

In the present work, the suitability of using Hal nanotubes–water nanofluids as heat transfer fluids is studied. To the best of our knowledge this is the first work using Hal as a nanoparticle for obtaining a nanofluid to be used in heat transfer applications. The solid powder was first characterized by means of SEM, TEM, WAXS, FTIR and TGA. Then nanofluids at different nanoparticle volume fractions (from 0.5 to 5%) were prepared and their thermal conductivity, specific heat and

viscosity were measured at different temperatures (40, 60 and 80 °C). In order to evaluate the suitability of this as a good heat transfer nanofluid the Prandtl number (Pr) was obtained. Prandtl number ($Pr = \eta_{nf} \cdot C_{p,nf}/k_{nf}$) compares thermal properties like specific heat ($C_{p,nf}$) and thermal conductivity (k_{nf}), with viscosity (η_{nf}). Experimental results showed that Hal nanotubes–water nanofluids present good characteristics to be considered as heat transfer fluids: high conductivity and moderate viscosity. Moreover, nanofluids were checked to remain stable for at least 24 h.

2. Materials and methods

2.1. Materials

Tests were carried out with Hal nanotubes. Chemical formula of Hal is $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, where $n = 0$–2. Anhydrous form of Hal ($n = 0$) has a basal spacing of 0.7 nm, while hydrated form ($n = 2$) has a basal spacing of 1 nm (Deen et al., 2012; Lvov et al., 2008; Rozynek et al., 2013). Outer surface of Hal nanotubes consists of tetrahedral siloxane groups (Si–O–Si), whereas inner consists of aluminol groups (Al–OH) (Alhuthali and Low, 2013; Kadi et al., 2012). Neighborhood of aluminol and siloxane layers provides a highly disordered structure with random dislocations and shifts, which rolls up the multilayer forming the hollow tubular form (Vergaro et al., 2010; Alhuthali and Low, 2013; Rozynek et al., 2013).

The powder used in this work was supplied by the U.S. company "NaturalNano, Inc." According to the manufacturer, Hal nanotube composition is between 98 and 99.8% of Hal. Hal nanotubes are ultra-tiny hollow tubes with diameters typically smaller than 100 nm, with lengths typically ranging from about 500 nm to over 1.2 μm.

Nanofluids with different volume concentrations (0.5, 1, 3 and 5%) were prepared by adding distilled water to the defined amounts of nanoparticles. In this method, known as the two-step method, the nanoparticles are purchased in dry powder and then dispersed in the liquid medium. The dispersion was made using an ultrasonic probe (HD2200 Sonopuls, Bandelin) and the mixture was submitted to a sonication treatment for 2 min. Afterwards, the pH of the nanofluid was modified by adding HCl or NaOH solutions (10% mass) in order to modify the surface charges of the particles and to electrostatically stabilize the dispersion. Finally, to ensure a correct dispersion of all the components, the nanofluids were submitted to a second sonication treatment during 2 min.

2.2. Experimental methods

Scanning electron microscopy (SEM) was performed in a Leica-Zeiss LEO 440 microscope equipped with digital image acquisition. Powder samples were observed so the morphology and size of the raw material were determined.

Transmission electron microscopy (TEM) images were obtained using a JEOL 2100 microscope at an operating voltage of 100 kV. TEM was used to observe the morphology and size of Hal nanotubes and clusters in the dispersion. In order to do this, a small amount of the sample was dropped on a copper grid and then was dried to remove the liquid. To prevent large agglomeration of particles during the drying of the sample very diluted nanofluids were prepared.

Wide angle X-ray scattering experiments (WAXS) were performed using a Bruker AXS D4 Endeavor diffractometer. Radial scans of intensity versus scattering angle (2θ) were recorded at room temperature in the range 2–30°2θ (step size = 0.02°2θ, scanning rate = 8 s/step) with identical setting of the instrument by using filtered CuKa radiation (λ = 1.54 Å), an operating voltage of 40 kV, and a filament current of 30 mA. To calculate the clay mineral d-value, Bragg's law (λ = 2d sin θ) was applied.

Fourier transform infrared (FTIR) spectra were collected for the Hal powder using a Jasco FT/IR-6200 spectrometer in attenuated total