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CHARACTERIZATION OF Cu AND Ni NANO-FLUIDS SYNTHESIZED BY PULSED WIRE EVAPORATION METHOD

In the present work, Cu and Ni nanofluids were synthesized using the pulsed wire evaporation (PWE) method in the different aqueous medias, namely (ethanol and ethylene glycol), and the effects of the aqueous media on the dispersion state, stability, and particle size of nanoparticles were studied. The size and morphology of synthesized nano-particles were investigated by transmission electron microscopy (TEM). Also, the dispersion stability of the nanofluids was evaluated by turbiscan analysis. The TEM results showed that the nano-particles were spherical in shape, and the average particle size was below 100 nm. The average particle size of the Cu nano-particles was smaller than that of Ni, which was attributed to a difference in the specific sublimation energy of the elements. Moreover, ethylene glycol (EG) exhibited higher suspension stability than ethanol. Finally, the dispersion stability of Cu@EG displayed the highest value due to lower particle size and greater viscosity.

Keywords: pulsed wire evaporation, nanofluid, Cu, Ni, suspension stability, dispersibility

1. Introduction

In recent years, nano-size materials have become attractive and important in industrial applications, because of their novel properties, which are not found in bulk-size materials. Basically, materials can be classified as bulk, powder, and thin film according to their shape or appearance. Among of these, nano-size metallic powders show great potential for use in a wide range of application areas, such as heat transfer, electronics, nuclear systems cooling, energy storage, solar absorption, friction reduction, and the biomedical field [1-4]. Although much research on the practical application of nano-size metallic powders has been carried out, their utilization is still limited because of their well-known disadvantages, such as low stability and the difficulty of handling nano-sized particles with a large specific surface area due to explosion and agglomeration. For these reasons, novel fabrication methods and technologies are needed for the stable usage of nano-size metallic powders.

In general, nanofluids can be classified in two groups in terms of their production method: one-step and two-step methods. The two-step method is the most frequently adopted method for preparing nanofluids. It involves first producing the dry powder by chemical or physical methods and then dispersing the powder into a fluid with the help of magnetic force agitation, ultra-sonic agitation [1], etc. Although the two-step method is useful for synthesizing nanoparticles, it still involves some disadvantages, such as process complexity, time consumption, production of hazardous substances, rapid surface oxidization, agglomeration between fine particles, impurities, etc. Likewise, since it is very difficult to prevent the full oxidation and agglomeration of nanoparticles in a gas atmosphere, the nanoparticles in this method have to be suspended in an aqueous medium, such as water, ethanol, ethylene glycol (EG), or oil.

In the one-step method, nanoparticles are produced and dispersed in fluid simultaneously. In this method, the processes of drying, storage, transportation, and dispersion of nanoparticles are not required, so more stable nanofluids in which the agglomeration of nanoparticles is minimized can be obtained. Pulsed wire evaporation (PWE) is one of the most promising one-step methods to obtain high quality, efficient, and low-cost nanofluids [5]. Compared to other processes involving several treatment steps, the PWE method has been recently developed to fabricate nano size particles or nanofluids. This process is capable of producing various metal and oxide nanoparticles by charging a starting wire in various gas (dry) and liquid (wet) media [6-11]. However, further research is still needed to optimize particle size and dispersibility control, since those properties can be easily affected by several process parameters, such as input voltage, material type, thickness of wire, aqueous media type, etc. In PWE process, the type of aqueous media plays a critical role not only on size and shape of particle but also on stability of suspension. This issue has been well addressed by some researchers on gold

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and silver nanofluids [12,13]. However, there are limited studies on Cu and Ni nanofluids.

In this study, we therefore focused on influence of aqueous media on the Cu and Ni nanofluids prepared by the newly developed high-energy pulsed wire evaporation (PWE) method. Two types of liquid, ethanol and ethylene glycol, were used as an aqueous media and their effects on the particle size and stability of the nanofluids were investigated using TEM, XRD and dispersion stability analysis.

2. Experimental procedure

High purity nanofluids were synthesized using the high-energy metal nano-colloidal manufacturing equipment (NTi 20PC, Nano Technology Co., Ltd.). The apparatus consists of four main components, a high voltage dc power supply, a capacitor bank, a high voltage gap switch, and an evaporation chamber. This apparatus is a newly developed PWE method to effectively fabricate various metals nano-colloidal by enhanced pulse energy (200J/pulse) with the attached ultrasonic dispersion device as compared to the conventional methods. High-purity copper (Cu) and nickel (Ni) wire (>99.8%) with a diameter of 0.3 mm was used as a starting material. The feed length of the wire per each explosion was set to 24~56 mm, and the number of explosions was 100 times. A high purity solution of ethyl alcohol (Ethanol) and ethylene glycol (EG) were filled into the chamber to prevent the oxidation and agglomeration of the powders. The synthesized nanoparticles were in direct contact with the solution inside the chamber, and then the nanofluid containing metallic nanoparticles was finally obtained. Hereafter, the final nanofluids were named as Cu@Ethanol, Ni@Ethanol, Cu@EG, Ni@EG for the sake of simplicity.

The crystal structures of the synthesized powders were determined by X-ray diffraction (XRD, MiniFlex600, RigaKu) using CuKα radiation (= 1.5406 A). The size, shape, and oxide layer of the powder were examined by high-resolution transmission electron microscopy (TEM, Tecnai G2 F30, FEI) with energy-dispersive X-ray spectroscopy (TEM-EDX). The measurement for dispersibility of the synthesized nanofluids was evaluated at 25°C through characterization of the delta BST and delta transmission properties obtained by dispersion stability analyzer (TURBISCAN Lab., TURBISCAN ageing station).

3. Results and discussion

Fig. 1 presents typical TEM images of the as-prepared Cu and Ni nanofluids in the different solvents. The micrographs reveal that all nanoparticles were spherical in shape. It is clearly seen that the Cu and Ni nanoparticles were better dispersed in EG than in ethanol. On the other hand, the agglomeration tendency of Ni nanoparticles was higher than that of Cu nanoparticles in both solvents. This can be attributed to the differences in magnetic properties of Cu and Ni. Cu is a diamagnetic material and unless an external magnetic field is applied, its net magnetic moment is zero and it has no magnetism. On the other hand, Ni is a ferromagnetic material and even though there is no external magnetic field, each domain in Ni has a net magnetic moment. So, a ferromagnetic nanoparticle behave as a tiny magnet since each particle consists of a few domain, mostly one domain, and apply attraction force to another particle. Hence, agglomeration tendency of Ni nanoparticles is expected to be higher than that of Cu. The overall size of the agglomerated particles ranged from 10 to 50 nm, and a few larger particles of 100 nm were observed for Ni as shown Figs.1 (b) and (d). The spherical shape of the particles may be due to minimized surface energy, whereas the aggregation of particles resulted from covalent interaction between small particles, collision, and coalescence during the formation process. The TEM results indicate that the particle size of Cu was substantially smaller than that of Ni nanoparticles in both solvent. In the PWE method, the particle size of materials depends on superheating factor, K. The value of K is determined by the following equation:

$$K = \frac{W}{W_s} \tag{1}$$

Where W is the energy introduced per gram of metal, and W_s is the sublimation energy per gram of metal. The sublimation energy values of Cu and Ni are 33 and 53.9 J/mm^3, respectively [8,14]. It is easily understood from equation 1 that the superheating factor K of Cu is higher than that of Ni due to lower W_s of Cu for the same W. Thus, the particle size of Cu is expected to be smaller than that of Ni because the liquid phase or semi solid phase was possibly condensed for Ni. This finding is in good agreement with previously published results, in which the particle size decreases (or the specific surface area increment) with increasing expansion rate and number of condensed center according to increasing K value. Also, as seen in Fig. 1, in comparison to ethanol, EG provided better dispersion and prevented clustering to some extent for both metals. Although ethanol and EG are classified as polar solvents, the polarity of EG is higher than that of ethanol, therefore, the dispersion ability of EG is expected to be better than that of ethanol. TEM images revealed that the combination of Cu and EG led to the finer particle size and better dispersibility.

The XRD patterns of the Cu and Ni nanoparticles are shown in Fig. 2. Their characteristic peaks can be indexed to those of pure face-centered cubic (fcc) Cu and Ni, corresponding to the (111), (200) and (220) planes, respectively. No additional impurity peak such as oxide was found. It is hard to detect the oxide phase by the X-ray diffraction method because the oxide layer is a very thin and amorphous structure. In order to determine such an impurity phase, TEM and TEM-EDX were carried out.

Fig. 3 clearly shows the thin coating layers of a few nm on the surface of all particles. The TEM-EDX results indicate that the nanoparticles were coated with a thin oxide layer of about <1~3 nm. The thickness of the oxide layers varies according to particle size. However, it is difficult to determine whether the

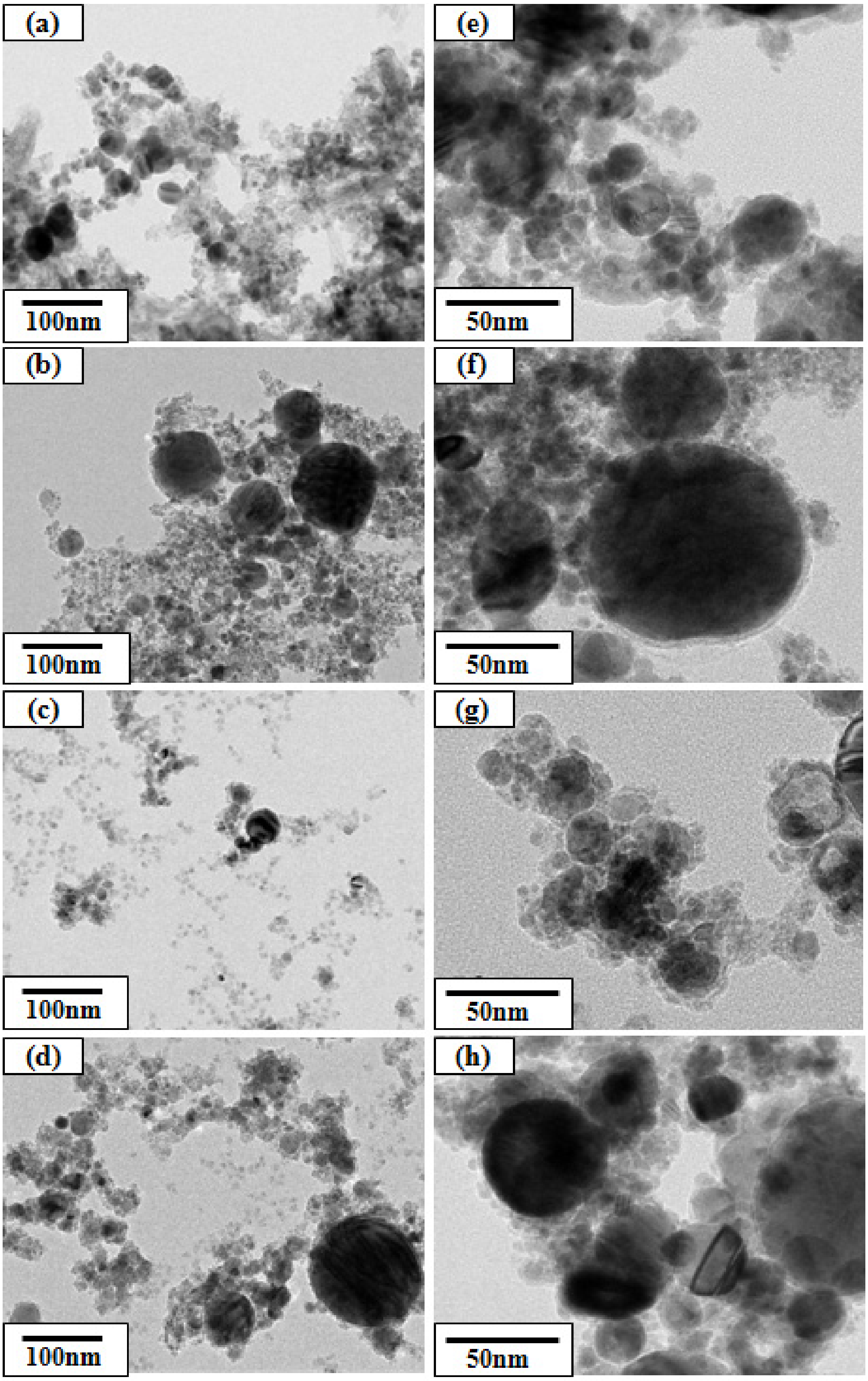

Fig. 1. TEM images of the nanofluids at low magnification: (a) Cu@Ethanol, (b) Ni@Ethanol, (c) Cu@EG, and (d) Ni@EG; and at high magnification: (e) Cu@Ethanol, (f) Ni@Ethanol, (g) Cu@EG, and (h) Ni@EG

thickness of the oxide layers depends on the type of metal (Cu, Ni) or the dispersant (ethanol, EG), which means that their effects are not obvious. Although, the nanoparticles were synthesized in liquid media, the oxide layers may have been formed by oxygen gas released from instantaneous plasma/vapor during the explosion of wire.

Fig. 4 displays the photograph captures obtained to observe this sedimentation state of nanofluids after preparation and the elapsed time of 20 days. After 20 days, both the Cu and Ni nanofluids in EG solution showed a homogeneous appearance without any visible settlement (Fig. 4b). By contrast, the nanoparticles in ethanol solution exhibited full settling at the bottom

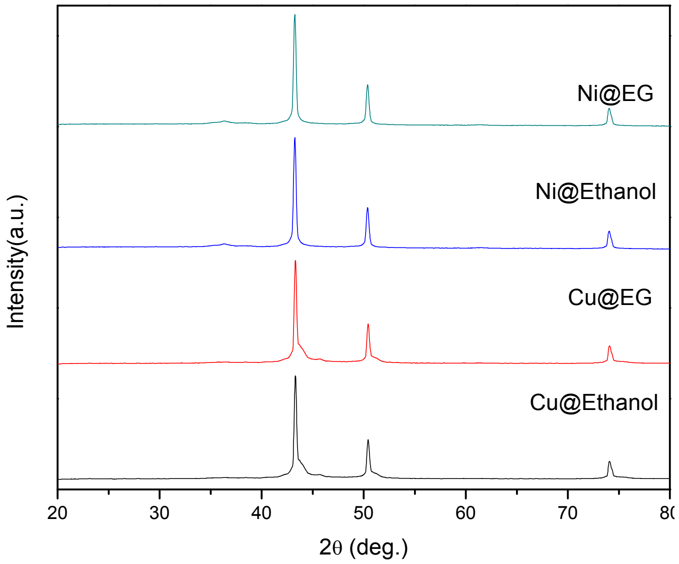

Fig. 2. XRD Patterns for Cu and Ni nanoparticles synthesized in ethanol/EG solvent

of the vials after 20 days. As seen in Fig. 4a, immediately after preparation, both Cu and Ni nanoparticles in ethanol solution have the tendency to settle. These visual observations together with TEM images indicate the higher contribution of EG to the separation of nanoparticles and prevention of aggregates between small particles in comparison to Ethanol.

The dispersion state and the long-term stability of each sample were examined more quantitatively with delta BST and delta T by turbiscan analyzer as shown Fig. 5. As seen in Fig. 5, Cu@EG displays no variation of transmission or back scattering over the 20 days of analysis, which demonstrates that the sample is highly stable. Ni@EG, however, showed slight sedimentation until 20 days, and then almost no change. The curves clearly indicate that the dispersion of Cu is better than that of Ni in EG, suggesting that the suspension stability is influenced by particle size. On the contrary, the nanoparticles synthesized in ethanol displayed a faster increment of curves in the same period of time, which demonstrates that the nanoparticles were unsteady and underwent quicker sedimentation. This behavior is due to the aggregation of nanoparticles as seen in Fig. 1. Such an observation reveals the better performance of EG as a dispersant compared to ethanol to prevent aggregation and to increase the separation of nanoparticles into smaller particles. Likewise, the Cu > Ni in ethanol confirmed a similar tendency comparison Cu > Ni in EG.

This behavior can be explained in terms of two important factors: particle size and viscosity.

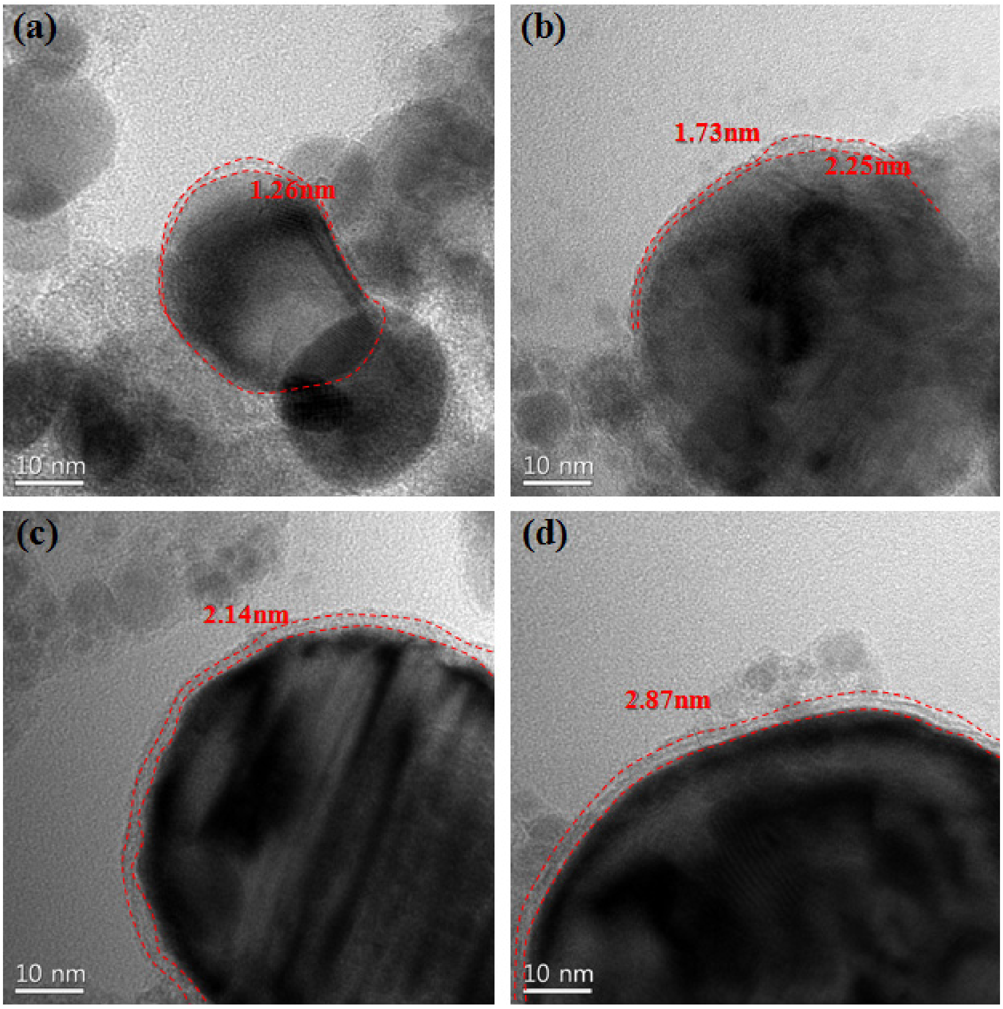

Fig. 3. TEM image of coating layer on the surface of Cu@EG particles synthesized by PWE at various particle sizes

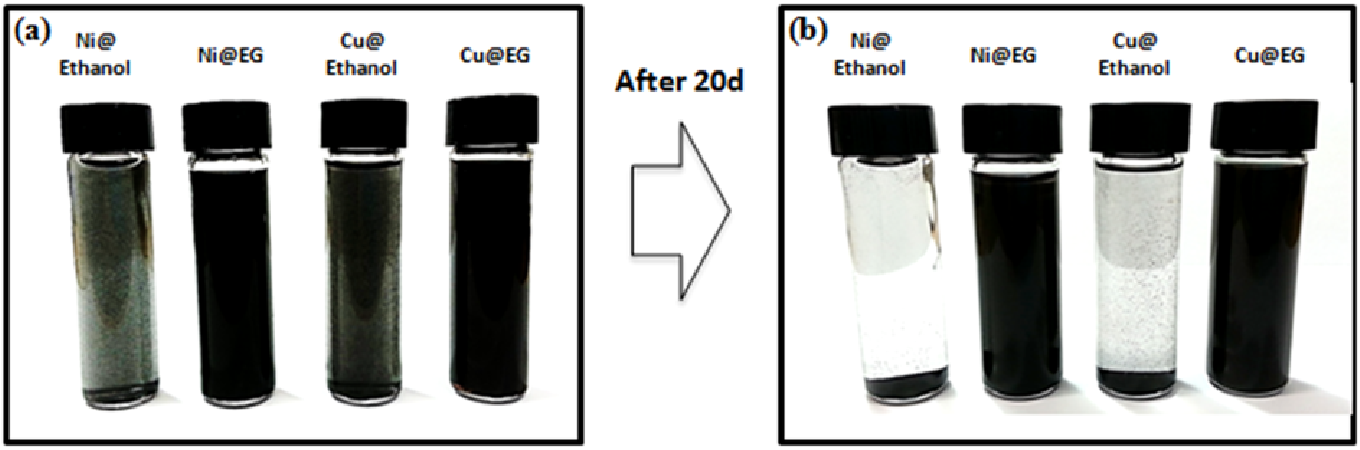

Fig. 4. The suspension stability of nanofluids (a) immediately after preparation and (b) after 20 days had elapsed

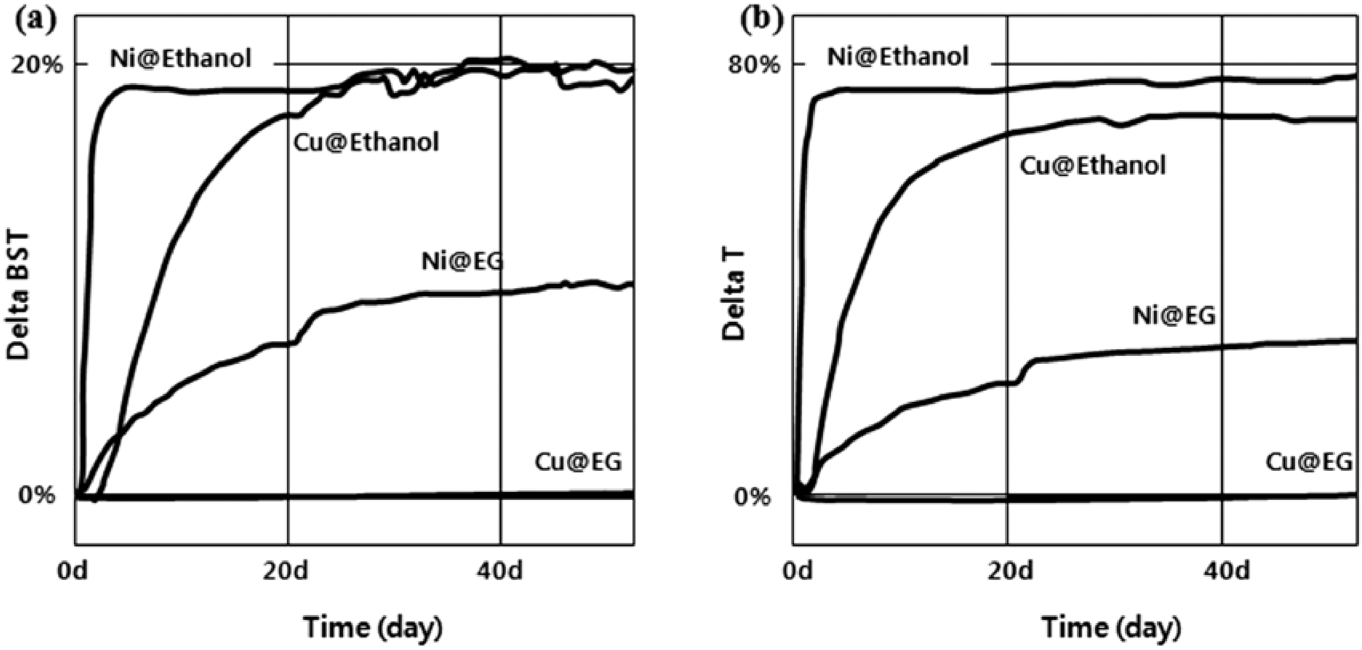

Fig. 5. Suspension stability with different preparation conditions; (a) delta back scattering transmission and (b) delta transmission

According to the Brownian forces equation [15],

$$\frac{a^4 \Delta\rho g}{k_B T} \tag{2}$$

where a is the particle radius, $\Delta\rho$ is the density difference between particles and liquid medium, g is the acceleration due to gravity, k_B is the Boltzmann constant and T is the temperature. It is well known that the gravity affects larger particles more than small particles, resulting in the sedimentation of larger particles. Moreover, during the PWE process, the particles will continually collide with each other; consequently, particles may aggregate due to Van der Waals attractive forces. This can lead to the formation of secondary particles with much larger size, which means a higher additional gravitational force, according to equation 2, finally resulting in sedimentation. In addition to particle size, viscosity is another factor, in which an increase in viscosity enhances the kinetic stability of the suspension. In a stationary state, the sedimentation velocity of small particles can be estimated from the Stokes's law [16]:

$$V = \frac{2\Delta\rho g a^2}{9\eta} \tag{3}$$

where V and η represent the sedimentation velocity and shear viscosity of the liquid medium, respectively. Here, $\Delta\rho$ and a are the same as those in Eq. 2. According to Eq. 3, to reduce the sedimentation velocity of nanoparticles and to obtain stable nanofluids, one should reduce the size of nanoparticles and increase the base fluid viscosity or minimize the density difference between nanoparticles and the base fluid. Therefore, the more the viscosity is increased, the more the rate of sedimentation is reduced. The viscosity of EG is about 16 times higher than that of ethanol, which results in the remarkable performance of EG to improve the stability. It also follows from Eq. 2 that decreasing in particle size will reduce the sedimentation rate and improve the stability of nanofluids. It is understood from Figs 4 and 5, however that the viscosity of liquid medium is the dominating factor rather than particle size.

In realistic industrial applications, nanofluids should possess some key properties: low viscosity to protect the pumping system, smaller nanoparticles to increase surface area, and less sedimentation to improve the efficiency of heat exchangers. In this context, Cu and Ni nanofluids in EG solution exhibits the optimum property for practical application since they have high long-term stability and smaller particle size. Because of their low viscosity, Cu and Ni nanofluids in ethanol solution also have potential for practical application, provided that their stability is increased by electrostatic, steric, or electrosteric stabilizing methods.

4. Conclusions

A novel one-step method, PWE, for preparing Cu and Ni nanofluids with high-purity in ethanol and EG was successfully performed. The particle size of the Cu nanoparticles was smaller than that of Ni in both solvents because of its higher superheating factor. TEM images showed that the size of both the Cu and Ni nanoparticles in EG was slightly smaller than that in ethanol, suggesting the effect of solution type on the particle size is not very strong. Similarly, the agglomeration tendency of the nanoparticles in EG was found to be lower than that of the nanoparticles in ethanol, which can be attributed to the higher polarity of EG. The Cu nanoparticles prepared in EG solvent displayed the highest long-term stability among all of the nanofluids studied. The stability of the nanoparticles was explained according to the Brownian motion and Stoke's law. Based on these results, we suggest that the stability of nanoparticles mainly depends on the viscosity of solvents.

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