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Characterization of carbon nanofluids applicable to heat transfer fluids

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열전달 유체 적용을 위한 카본 나노유체 특성 분석

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Abstract

The carbon laden suspensions in water with no surfactants have poor stability caused by the hydrophobic layer of particles. In this study, the water-based carbon nano colloide(CNC) was successfully produced using electro-chemical one-step method without agent. The properties of CNC were characterized by using various techniques such as particle size analyzer, TEM, FT-IR, turbidity meter, viscometer, and transient hot-wire method. The average size of the suspended in the CNC was 15 nm in diameter. The thermal conductivity of CNC compared with water was increased up to 14% with 4.2wt% concentration. The CNC was stable over 600hr. The enhanced colloidal stability of CNC may be caused by the chemical structures, such as, hydroxide and carboxyl groups formed in outer atomic layer of carbon, which (i) made the carbon nanofparticles hydrophilic and (ii) prevented the aggregation among nanoparticles.

1. Introduction

Nanotechnology is an important field at the crossroads of physics, engineering, and materials science. Especially, carbon nanostructures including carbon nanotube (CNT) and fullerene (C60) have attracted much interest because of their potential applications in display, heat transfer media, fuel cell, functional composite materials, and anti-wear materials. However the applications of CNT and fullerene are limited because they are easily aggregated each other due to strong van der Waals attraction forces. To obtain the stable dispersion of CNTs in an aqueous solution, an additive or chemical reagent is generally required[1].

Hudson et al. and Peckett et al. found that colloidal graphite was able to be obtained by an electrochemical oxidation method, which involves the anodic erosion in the mixture of ethanoic acid, sulfuric acid, and deionized water[2, 3].

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In this paper, we describe an electrochemical and sonochemical oxidation method to produce the water-based carbon nano colloid (CNC) with excellent stability. The morphology and size distribution of CNC prepared in this study was analyzed by using a TEM and a particle sizer.. Since the nanofluids such as CNC are the new engineering materials, we also measured the thermal conductivity and viscosity of CNC for their potential applications in heat transfer-enhanced systems. Turbidity analysis was also made to evaluate the colloidal stability of aqueous suspension. To investigate the stabilization mechanism of CNC prepared, FT-IR spectroscopy and zeta potential analysis were made.

2. Experimental

2.1 One-step electrochemical method for CNC preparation

High density isotropic graphite was used as an anode and a stainless steel plate was used as a cathode. In the electrolysis process, the electric power applied to the electrodes was varied in multiple stages. Simultaneously, the colloidal solution was forcedly dispersed by an ultrasonica-

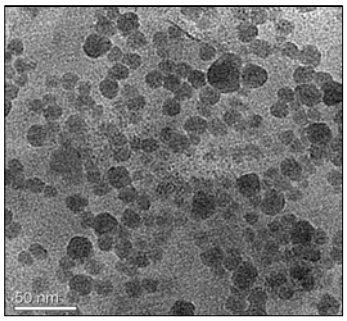

Fig. 1 TEM image of electrochemically produced carbon nano colloid (CNC).

-tor. The combined electrochemical and sonochemical oxidation processes were kept for 30 days, and then the saturated concentration of CNC was found to be ~0.4 wt%. We also monitored the electrical conductivity of the D.I. water using a electrical conductivity meter (LF11, SCHOTT) during the electrolysis process where the electrode was eroded to generate CNC.

2.2 Characterization of physical, chemical, and thermal properties of CNC

The morphology of CNC was determined by a TEM analysis (JEMM 2011, Jeol). The FT-IR spectra were also measured by a Perkin Elmer Spetrum GX spectrometer. Particle size distribution and zeta potential of CNC were measured by a dynamic light scattering and an electrophoretic light scattering (ELS-8000, Otsuka Electronics) technique, respectively. For evaluating the colloidal stability, the turbidity of CNC was measured as a function of sedimentation time with the assistance of nephelometer (2100AN, HACH). To measure the thermal conductivity of CNC, a transient hot-wire method was employed. Teflon-coated platinum wire with the diameter of 76 ㎛ and the length of 15 cm was used for thermal conductivity measurement based on the hot wire method. The viscosity of CNC was measured by Ubbelohde viscometer (Capillary viscometer with viscoclock, SCHOTT).

3. Results and discussion

3.1 Morphology and particle size distribution measurements of CNC

Fig. 1 shows the TEM image of CNC. One can see that the nanoparticles are spherical shape with the average diameter of ~15 nm. The size distribution of primary particles in the CNC was measured by using a dynamic light scattering measurement technique was presented in Fig. 2.

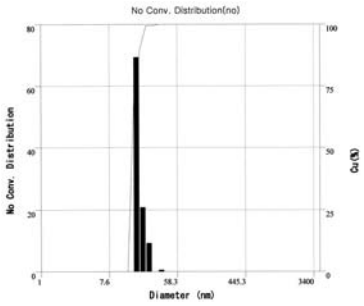

Fig. 2 Particle size distribution of CNC at 25°C and pH = 2.3.

The average size of primary particles was found to be ~18 nm with very narrow particle size distribution.

3.2 Measurement of thermophysical propertyies of CNC

To evaluate the heat transfer performance of CNC, we needed to measure its effective thermal conductivity and viscosity. Fig. 3 shows the thermal conductivity enhancement of CNC compared with pure water. As the CNC concentration was increased from 0.4 wt% to 4.2 wt%, the thermal conductivity enhancement of CNC was observed to increase from 2% to 14%. In the rheological study, the viscosity of CNC with various concentrations and temperatures was measured as shown in Fig. 4. The viscosity of CNC was decreased with increasing the fluid temperature, and simultaneously it was increased with increasing the colloidal concentration. Also it is interesting to note that the viscosity of CNC with the concentration of even ~6 wt% was increased only ~15% compared with that of D.I. water. Since the increase of viscosity in nanofluids is generally resulted from anchoring between the aggregated particles in the nanofluids, this indirectly implies that the carbon nanoparticles in our CNC nanofluid were well separated by strong repulsion forces with even high concentration of nanoparticles (i.e. ~6 wt%).

3.3 Stability test of CNC

The stability of the ceramic suspension is generally determined by measuring the sediment volume as a function of time. However, this method is not suitable for our current CNC suspension because the CNC was too dark to detect the volume of sediment. Therefore the supernatant was analyzed in this approach for qualitatively evaluating the stability of CNC suspension by using a turbidity meter. It was observed to be very stable without any abrupt

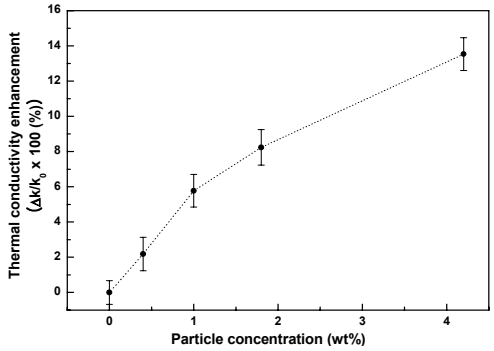

Fig. 3 Thermal conductivity enhancement of CNC as a function of particle concentration at 25°C and pH = 2.3.

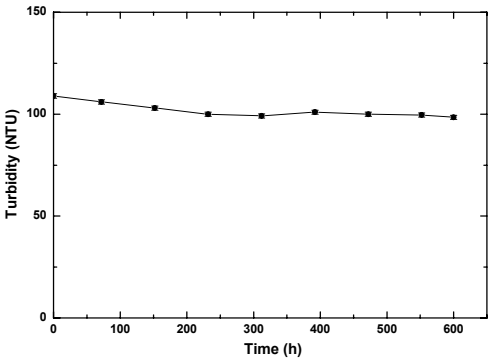

Fig. 5 Evolution of turbidity as a function of elapsed time for the 0.2wt% CNC.

changes in the turbidity values for 600 hours as seen in Fig. 5, indicating that the diluted CNC was very stable.

3.4 FT-IR Spectrometer analysis of CNC

We performed FT-IR measurement for the original graphite electrode, the as-produced CNCs at pH = 2.3 and pH = 5.1, and the dried CNC nanoparticles. The FT-IR spectrum of the original graphite electrode prior to oxidation (i.e. spectrum (a) in Fig. 6) shows no significant bands except the weak absorption band at 1697 cm^{-1} probably owing to impurities in the potassium bromide. Spectrum (b) and (c) in Fig. 6 shows the original CNC prepared at different pHs. Both spectrum (b) and (c) similarly shows the absorption bands at 3367 cm^{-1} and 1639 cm^{-1}. Spectrum (d) in Figure 8 presents the carbon nanoparticles, which were dried at 100°C for 24 hours. The strong transmittance signals appeared at 3458 cm^{-1}, 1712 cm^{-1}, 1252 cm^{-1} and 1450 cm^{-1} are occurred due to O-H, C=O, C-O stretching, and O-H bending, respectively. Another strong band at 1632 cm^{-1} is presumably occurred due to the C=C stretching of graphite. The border and strong peak from 2300 cm^{-1} to 3500 cm^{-1} show the O-H stretching due to the presence of hydroxyl group, and also the

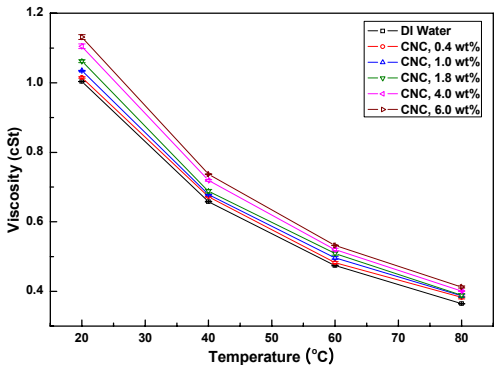

Fig. 4 Viscosity of CNC at different concentrations as a function of temperature.

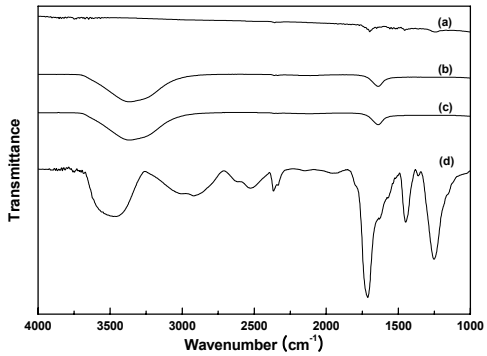

Fig. 6. FT-IR spectra of (a) the original graphite electrode, (b)electrochemically produced CNC with pH = 2.3, (c) CNC with pH=5.1, and (d) dried CNC under 100 °C for 24 hours.

strong peak of 1712 cm^{-1} shows the presence of carbonyl group. The carboxyl group combined with hydroxyl and carbonyl group are known as hydrophilic functional groups. We believe that the formation of hydrophilic functional groups on the surface of the carbon nanoparticles eventually resulted in the induction of strong repulsion forces among the primary carbon nanoparticles.

3.5 Possible mechanism of the formation of stable CNC

The functional groups such as carbonyl, hydroxyl and carboxyl group were formed on surface of carbon nanoparticles verified by FT-IR analysis. A schematic representation of the graphite surface oxides was presented in Fig. 7. In the graphite structure, each carbon atom is covalently bonded to other carbon atoms so that they form flat sheet-like sequential hexagonal structures. However the parallel flat sheets of hexagonal structured carbon atoms are weakly bonded together by van der Waals attraction forces, implying that the parallel carbon flat sheets are easy to split by relatively weak external forces, and also other functional groups can easily enter between the graphite flat

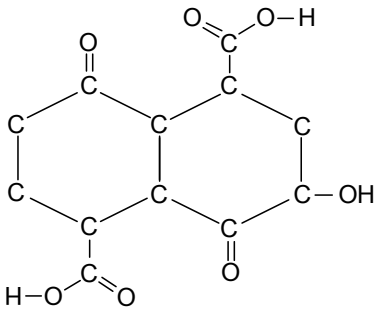

Fig. 7 The functional groups of graphite surface in the electrochemical oxidization process.

sheets[4]. On the basis of graphite structures, we describe the mechanism of the formation of stable CNC as seen in Fig. 8, which presents the schematic of CNC production process in the electrochemical and sonochemical oxidization. Initially, the stacked layers of the graphite at the electrodes were bonded together by van der Waals attraction force (see Figure 10(a)). During the electrochemical oxidization in the water, an anion (OH-) formed from the cathode with the excess of electrons moved toward the anode with the deficit of electrons. At the anode, the electrons were removed at the surface of carbon nanoparticles, and simultaneously the oxidation process was occurred. Furthermore the ultrasonic treatment during the electrochemical process added cavitations energy on the surface of carbon nanoparticles for enhancing the dispersity. Since the combined oxidation and cavitations energy were imposed on the surface of carbon in the electrochemical process, the magnitude of repulsion forces formed between the stacked layers get larger than that of van der Waals attraction forces between the layers as depicted in Figure 10(b) so that the resulting CNC nanofluid is able to maintain its stability as long as the hydrophilic functional groups exist.

4. Conclusion

With the assistance of a one-step electrochemical oxidization method, the ultra stable aqueous CNC solution was successfully produced without adding any surfactants in this study. Various characterization techniques were employed to measure the physical, chemical, and thermal properties of the CNC by using TEM, particle sizer, FT-IR, zeta meter, transient hot-wire, and viscometer. We found that the formation of the hydrophilic functional groups on the surface of carbon nanoparticles in the CNC solution, which eventually resulted in the excellent stability of the resulting CNC suspension in D.I. water. As a

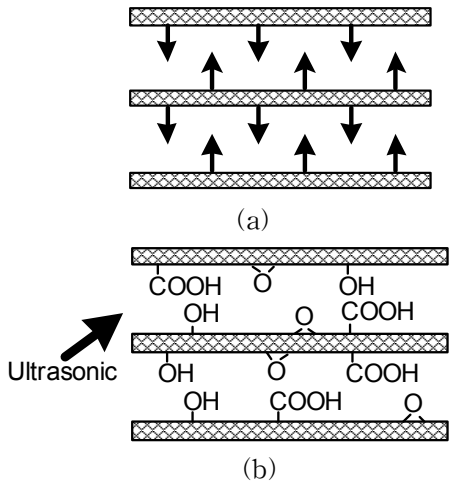

Fig. 8 The schematic of CNC production process in the electrochemical and sonochemical oxidization. (a) van der Waals attraction forces acting between the stacked layers in graphite and (b) functional groups-induced repulsion forces acting between the stacked layer in graphite.

result of stability test, we confirmed that CNC is well dispersed in the D.I. water over a long time period upto ~600 hours. Also the thermal conductivity of the CNC prepared with the initial concentration of ~4.2 wt% was enhanced ~14% compared with the thermal conductivity of pure water.

Ackonwledgement

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