PREPARATION OF SILICA-COATED MWNTS AND THEIR ADDITION TO SHEAR THICKENING FLUID OF SILICA/PEG SUSPENSION

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1 Introduction

Shear thickening is a non-Newtonian flow behavior observed by an increasing viscosity with increasing shear stress rate [1]. A typical shear thickening fluid (STF) is colloidal silica particles dispersed in polyethylene glycol (PEG) at a particular ratio. Lee et al [2] explained the reversible shear thickening phenomenon of colloidal suspension of silica in PEG. STF can be used for protective materials at a high shear rate such as a bulletproof vest. However, the brittleness and low resistance to mechanical stress of silica reduced the performance of the silica/PEG STF. To overcome this problem, Kalman et al [3] studied the effect of particle hardness in STF on ballistic penetration by using poly(methyl methacrylate) nanoparticles instead of silica particles. Among the various methods to enhance protective performance of the silica/PEG STF, multi-walled carbon nanotubes (MWNTs) would be used as additional nanofillers since they exhibit excellent mechanical properties [4]. However, the effects of the MWNT addition to silica/PEG suspenion are not expected to be good due to the low dispersibility of MWNT in the suspension media.

In this study, silica coating on the MWNT surface through covalent bonding [5] was used to increase the dispersibility of MWNT in silica/PEG STF suspension. Amino group-introduced MWNT (MWNT-NH_2) was prepared first and various amount of silica was subjected to forming on the surface of MWNT-NH_2 by using a sol-gel method [6]. The silica formation on the MWNT surface was analyzed using various instruments. Changes in rheological properties of silica/PEG STF according to the addition of silica-coated MWNT (Si-MWNT) were also investigated.

2 Experimental

2.1 Materials

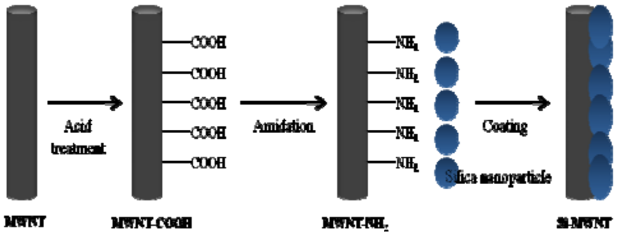
MWNT was the product of Carbon Nanotech Co. (Korea). 1-Ethyl-3-(3-dimethylaminopropyl)carbo-diimide hydrochloride (EDC) and N-hydroxy-succinimide (NHS) were purchased from Aldrich (USA), and ethylene diamine (ED) and tetraethyl orthosilicate (TEOS) from Tokyo Chemical Inc (Japan). Other reagents such as PEG(#200), N,N-dimethylformamide (DMF), and ethanol were of reagent grade. All the reagents were used as received.

2.2 Modification of MWNT Surface

Carboxylic groups were introduced on MWNT first by treating MWNT in concentrated H_2SO_4/HNO_3 (3:1, v/v) at 60°C for 2 hours. Then MWNT-NH_2 was prepared by a reaction of the acid-treated MWNT (MWNT-COOH) with ED using EDC and NHS as catalysts in DMF at room temperature, followed by filtering, rinsing, and drying. The reaction time, amount of ED and catalysts (EDC and NHS) were varied to find an optimum condition for the preparation of MWNT-NH_2.

2.3 Synthesis of Si-MWNT and Silica Nanoparticles

MWNT-NH_2 with a nitrogen atom content of 20 wt % was reacted with various amounts of TEOS (0.2~100:1, weight ratio to MWNT) with mechanical stirring in water/ethanol/ammonia water solution (10:12:2, v/v/v) at room temperature for 3 hours. Filtration of the precipitates, washing with water, and drying at 100 °C for 12 hours finally gave Si-MWNT. Scheme 1 shows schematic diagram to obtain MWNT-COOH, MWNT-NH_2, and Si-MWNT.



Scheme 1. Schematic diagram for the synthesis of Si-MWNT via a three step process.

Silica nanoparticles were also synthesized by the same method as above without using MWNT-NH_2 and they were used as dispersed particles for silica/PEG suspension.

2.4 Fabrication of STF containing Si-MWNT

After mixing silica nanoparticles and Si-MWNT in methanol with sonication for 24 hours, PEG was added to the mixture. Final suspension was prepared with further sonication for 24 hours and removal of methanol by drying.

2.5 Characterizations

Fourier Transform Infrared (FT-IR) spectrometer (FT/IR-6300, Jasco), Field Emission Scanning Electron Microscope/Energy Dispersive Spectrometer (FE-SEM/EDS; JSM-6700F, Jeol), Transmission Electron Microscope (TEM; JEM1010, Jeol), and Rheometer (AR2000ex, TA Instrument) were used to analyze the samples. Silica content of Si-MWNT was calculated from the comparison of weight residue of Si-MWNT and MWNT-COOH at 800°C in TGA curves.

3 Results and Discussion

The surface modification of MWNT (MWNT-COOH and MWNT-NH_2) and the introduction of silica on the MWNT surface were confirmed by the bands of carbonyl (1726 cm^{-1}), amine (3300 cm^{-1}), amide (1550, 1630 cm^{-1}), and Si-O-Si group (1090 cm^{-1}) in FT-IR spectra.

The morphological features of Si-MWNT observed by FE-SEM and TEM are shown in Figure 1 and Figure 2, respectively. With increasing the amount of TEOS at a fixed weight of MWNT-NH_2, silica was coated uniformly on the surface of MWNT-NH_2 and the thickness of silica-coated layer increased.

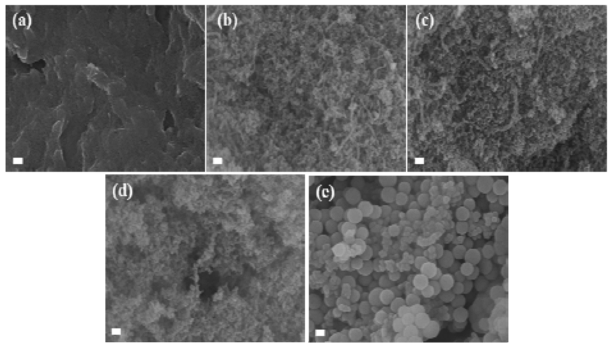


Fig. 1. FE-SEM images of Si-MWNT prepared with various amounts of TEOS. Weight ratio of TEOS to MWNT-NH_2; (a) 0.2, (b) 2, (c) 20, (d) 60, (e) 100. (scale bar=100 nm)

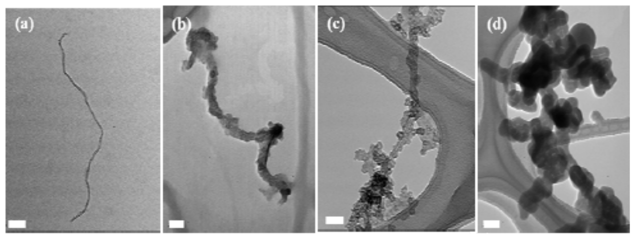


Fig. 2. TEM images of Si-MWNT prepared with various amounts of TEOS. Weight ratio of TEOS to MWNT-NH_2; (a) pristine MWNT, (b) 20, (c) 60, and (d) 100. (scale bar=50 nm)

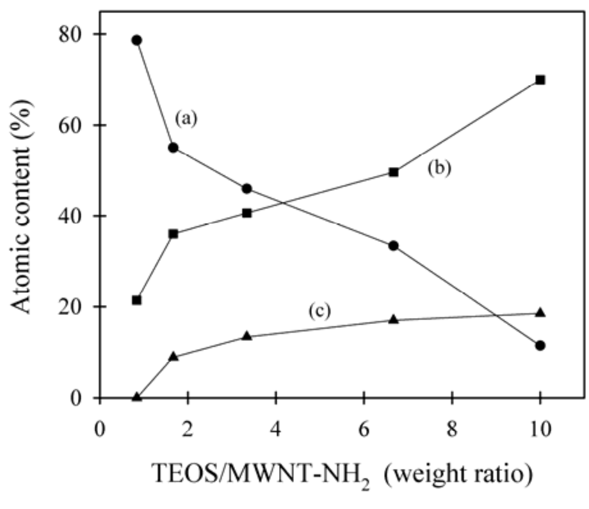


Fig. 3. Changes in (a) carbon, (b) oxygen, and (c) silicon atom content of Si-MWNT prepared with various weight ratios of TEOS to MWNT-NH_2.

From the analysis of EDS spectra of Si-MWNT, atom content of C, O, and Si were obtained. Figure 3 shows the changes in C, O, and Si atom content according to TEOS/MWNT ratio. Silicone and oxygen atom content increased and carbon atom content decreased with increasing the amount of TEOS, representing that the amount of silica increased.

In order to check the change in hydrophilicity with modification, MWNT-NH_2 and Si-MWNT along with pMWNT were dispersed in toluene/water mixture by sonication and observed for 7 days. Figure 4 shows the dispersion state after 7 days from sonication. Comparing the result that pMWNT was dispersed in toluene, MWNT-NH_2 was dispersed well in water due to the increased hydrophilicity. Si-MWNT was also dispersed well in water irrespective of the amount of silica. Meanwhile, it can be seen that the color of Si-MWNT changed from black to transparent as the amount of silica increased since the silica layer covered MWNT entirely. This would be helpful where the application of MWNT was limited because of its black color.

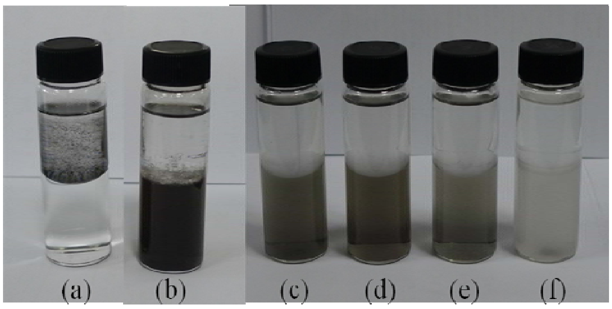


Fig. 4. Photographs showing dispersion stability of (a) pristine MWNT, (b) MWNT-NH_2, and (c-f) Si-MWNT in toluene(up)/water(down) prepared with various amounts of TEOS. Weight ratio of TEOS to MWNT-NH_2; (c) 2, (d) 20, (e) 60, and (f) 100.

Si-MWNTs with a silica content of 90% and 65 wt% prepared by a reaction of TEOS and MWNT-NH_2 with a weight ratio of 100:1 and 60:1, respectively, were used for further experiments.

Figure 5(a) shows shear rate dependence of viscosity of silica/PEG suspension with 65% colloidal particles, where a typical shear thickening phenomenon was observed beginning at a critical shear rate of 100 s^{-1}. This shear thickening behavior is explained by formation of flow induced cluster (hydroclusters) due to hydrodynamic forces [7]. When 3% silica was replaced with pMWNT, i.e., 3% pMWNT and 62% silica was used in PEG, the pMWNT was not dispersed in the suspension and no shear thickening phenomenon was observed, as shown in Figure 5(c). In this case, pMWNT obstructed making hydrodynamic forces due to the low dispersion in PEG. On the other hand, when 3% Si-MWNT with a silica content of 90% was used with 62% silica, the suspension showed a similar shear thickening behavior to simple silica/PEG system (Figure 5(b)). Although not shown in the figure, the critical shear thickening point of silica/Si-MWNT/PEG suspension moved to a lower shear rate with increasing Si-MWNT content.

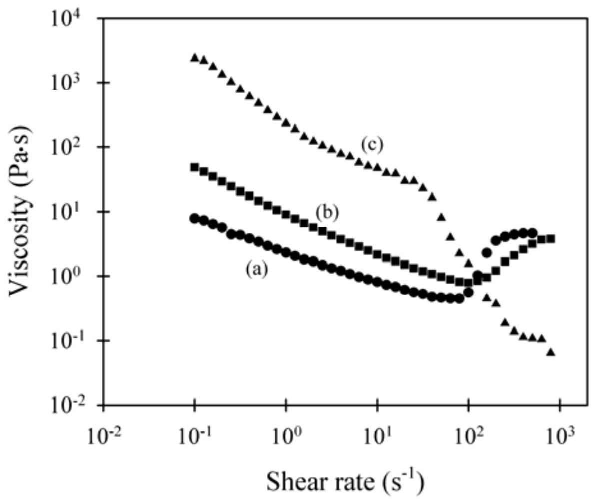


Fig. 5. Steady state viscosity curves PEG suspensions with 65 wt % particles; (a) silica/PEG (65/35), (b) silica/Si-MWNT (silica content of 90%)/PEG (62/3/35), and (c) silica/pMWNT/PEG (62/3/35).

Figure 6 shows the effect of the addition of Si-MWNT (silica content of 65%) to the silica/PEG (65/35) suspension on the shear rate dependence of viscosity for the complex suspensions. In this case, the addition of Si-MWNT causes an increase in total concentration of particles. As a whole, the viscosity level increased with increasing the amount of Si-MWNT and shear thinning at low shear rates was observed in all cases. When 1% Si-MWNT was added to the system, shear thickening behavior was observed at a lower critical shear rate compared to the simple silica/PEG system. It is reported that hydroclusters were formed at a low shear rate when high volume concentration of particles in PEG was used [8]. On the other hand, it was impossible to measure the viscosity at high shear rates when 3% and more Si-MWNT were added because of the highly increased viscosity of the system.

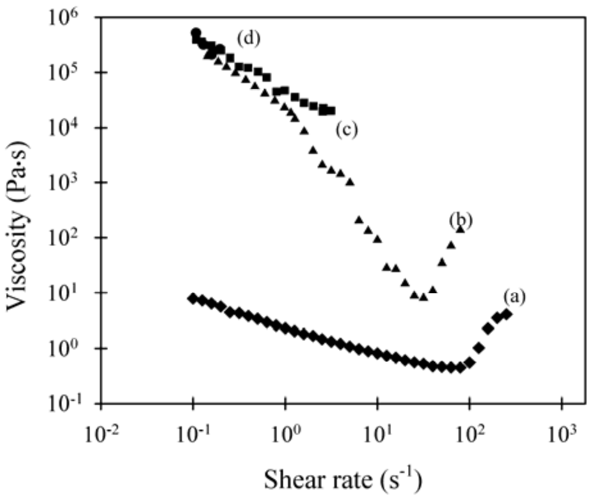


Fig. 6. Steady state viscosity curves for PEG suspensions containing (a) 65% silica, (b) 65% silica + 1% Si-MWNT, (c) 65% silica + 3% Si-MWNT, and (d) 65% silica + 5% Si-MWNT. The silica content of Si-MWNT is 65 wt%.

4 Conclusions

Silica-coated MWNT (Si-MWNT) with various contents of silica was prepared by using a sol-gel method and the effects of the addition of the Si-MWNT to silica/PEG (65/35) suspension on the shear thickening property were examined. MWNT-NH_2 was prepared first by reacting acid-treated MWNT and ED using EDC and NHS as catalysts, and then silica was subjected to forming on the surface of MWNT by a reaction with TEOS initiating from the amino groups of MWNT-NH_2. Comparing the result that shear thickening phenomenon disappeared when 3 wt % of pristine MWNT was added to silica/PEG suspension, the phenomenon was maintained when 3 wt% of Si-MWNT was added to the suspension. The critical shear thickening point of the Si-MWNT added suspension moved to a lower shear rate with increasing Si-MWNT amount.

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