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SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITE OF MULTI-WALLED CARBON NANOTUBE AND POLYANILINE NANOPARTICLE

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We synthesized multi-walled carbon nanotube (MWNT)/polyaniline (PANI) nanocomposites from an oxidative dispersion polymerization using poly (vinyl alcohol) (PVA) as a polymeric stabilizer. Purified MWNT whose metallic catalysts have been removed in acidic media was applied. The formation of nanocomposites and their morphology were confirmed by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electro-rheological properties were further characterized by a rotational rheometer equipped with a high voltage generator.

Keywords: multi-walled carbon nanotube; nanocomposite; polyaniline

INTRODUCTION

Recently, carbon nanotube (CNT)/polymer composites have been widely investigated due to unique properties of the CNT; a large aspect ratio, good electrical conductivity and thermal stability [1,2,3]. Industrial applications of CNT have been also diversified to many fields such as electronic devices and field emission display. The diameter of single walled carbon nanotube is 1.4 nm commonly, and that of MWNT is 10–60 nm with a layer distance between walls of 3.4 nm. Because of the electrical property of CNT,

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polymer/CNT composites can be applied as an electromagnetic shielding material. It has been also reported that the strength and thermal conductivity of conductive polymer increase about 3.5 and 2 times higher, respectively when the CNT has been added 1–2% in a conductive polymer matrix [4].

Concurrently, PANI is one of the best known conducting polymers for various electrochemical applications such as secondary battery, electromagnetic shielding material and flexible light emitting diode. Recently, the PANI has been also recognized as an electrorheological (ER) material [5]. An ER fluid is generally composed of a suspension of micron-sized semiconducting or conducting particles dispersed in an insulating fluid, which shows a rapid and reversible change of viscosity with an applied electric field [6].

We synthesized PANI nanocomposites from an oxidative dispersion polymerization using PVA as a polymeric stabilizer for dispersion of PANI. The MWNT/PANI nanocomposite was then prepared by applying ultrasonication following the similar procedure as PANI nanocomposite preparation. The shape difference of PANI and MWNT/PANI was observed by both SEM and TEM. The UV/VIS spectrophotometer was used for chemical analysis. We also used a rotational rheometer equipped with a high voltage generator for ER measurement.

EXPERIMENTAL

The MWNT (Iljin Nanotec Co., Korea) synthesized by a thermal chemical vapor deposition method was used. Since the purity of pristine MWNT was 97%, it was treated with HNO_3 at 60°C for 12 h, followed by a reflux process in HCl at 120°C for 6 h to eliminate impurities such as metallic catalysts. The purity of the treated MWNT was finally increased to be 99% based on thermogravimetric analysis (TGA) measurement. The acid-treated MWNT (5wt% for aniline) was added in a liquid state of aniline monomer. MWNTs are in general difficult to be uniformly dispersed in most solutions as they have large surface areas and possess large van der Waals forces among themselves. So an ultrasonication method was applied to the MWNT dispersion using an ultrasonic generator [7]. PVA used as surfactant was dissolved in deionized water. Aqueous HCl and aniline with MWNT were added to the solution and stirred with ultrasonication until it approached 10°C. Then deionized water containing ammonium peroxydisulfate was added through dropping, with continuous stirring and ultrasonication for 24 h at 10°C. The polymerized MWNT/PANI was separated by centrifugation at 7000 rpm for 0.5 h by three times.

Both SEM and TEM were used to observe the shape and size of the MWNT/PANI nanocomposites. Absorption spectra for $\pi-\pi^*$ transition of

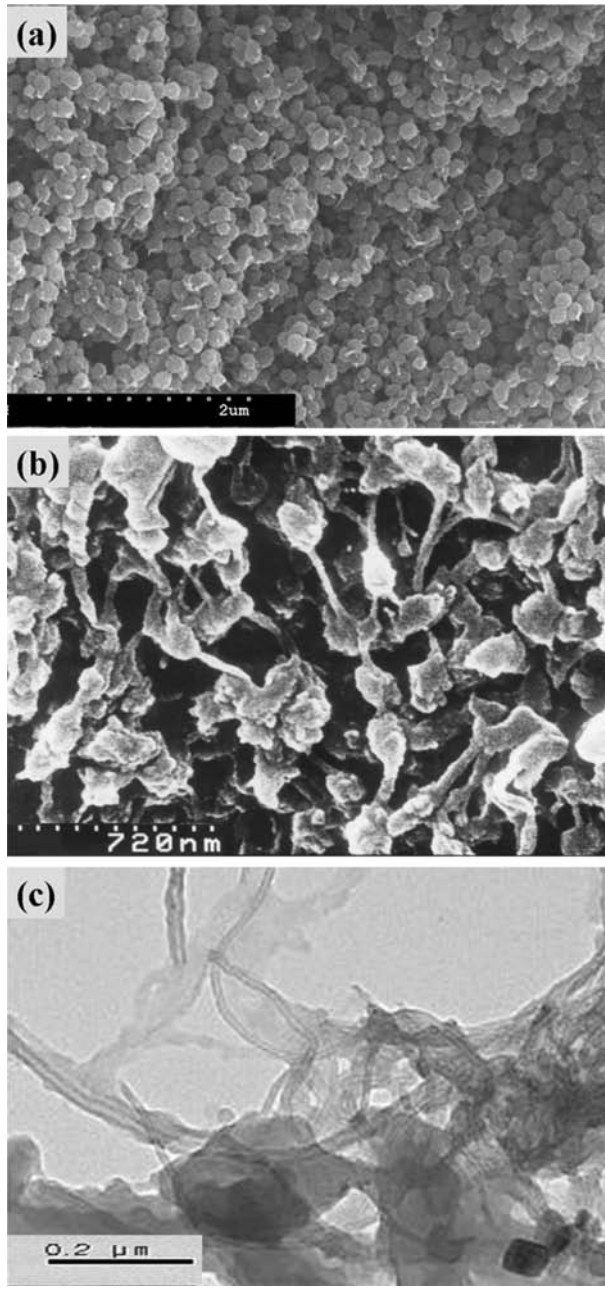

FIGURE 1 SEM image of (a) PANI nanoparticle, (b) MWNT/PANI nanocomposite and TEM image (c) of MWNT/PANI nanocomposite.

PANI were measured by UV/VIS spectrophotometer, and conductivity was also measured by four-probe method.

Finally, flow curve of MWNT/PANI nanocomposites based ER fluid was measured by a rotational rheometer (Physica, MCR 120) equipped with a high DC voltage generator.

RESULTS AND DISCUSSION

The rate balance between PANI polymerization and adsorption of stabilizer PVA determines the shape and size of PANI nanocomposites during the synthesis [8]. A spherical shape is observed when the adsorption rate of the stabilizer PVA exceeds the rate of PANI polymerization. Figure 1(a) shows PANI nanoparticles having a spherical shape with a uniform size. This PANI nanoparticles are well dispersed in water medium and no sedimentation is observed for a few weeks, indicating that the PVA was stably adsorbed onto the surface of PANI. In the case of MWNT/PANI nanocomposites (Fig. 1(b) and (c)), PANI seems to be pierced with MWNT like a

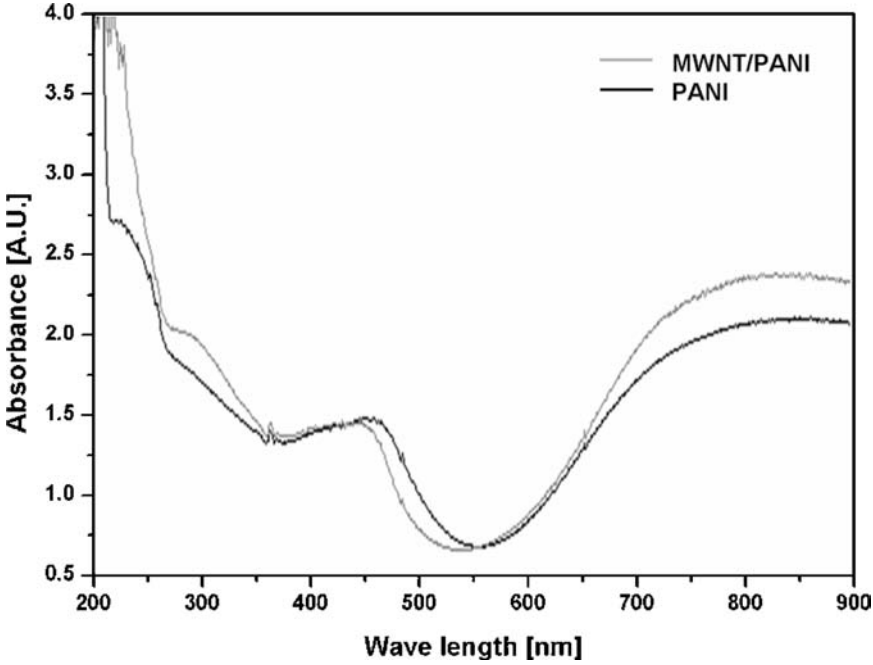

FIGURE 2 UV/Visible absorption spectra for both PANI and MWNT/PANT nanoparticles.

kebab structure. As the MWNT was added in the composites, the shape of PANI became oval.

Figure 2 gives UV/Visible absorption spectra for both PANI and MWNT/PANI nanoparticles. The absorption peaks at 460 nm and 800 nm wavelength are $\pi-\pi^*$ transition of benzenoid rings and $\pi-\pi^*$ transition of quinoid ring which belongs to PANI chain of PANI and MWNT/PANI nanocomposites. The absorption peaks of this doped PANI with HCl dopant were shifted to a longer wavelength compared with undoped PANI salt. At a wavelength of 800 nm, the peak of MWNT/PANI nanocomposites is quite higher than PANI nanocomposites. The higher absorption of MWNT/PANI nanocomposites means that there are more quinoid ring than PANI nanocomposites without MWNT. We can suppose that MWNT affects a generation of polaron band in the PANI emeraldine chains.

Figure 3 represents flow curve of shear stress vs. shear rate for MWNT/PANI suspension in insulating silicone oil under an applied DC electric field strength. Before applying the shear, a DC electric field was maintained during 3 min for an equilibrium columnar structure. In the absence

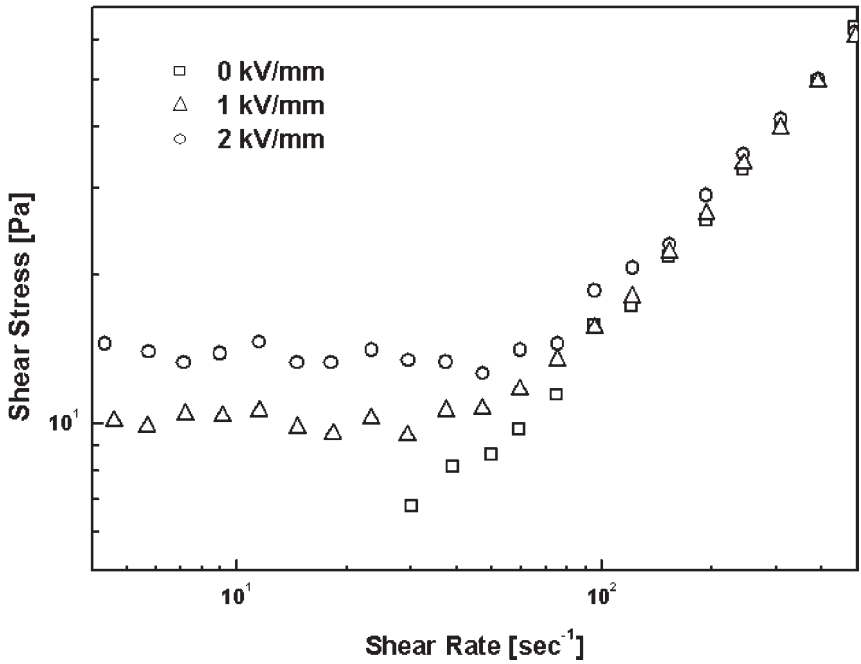

FIGURE 3 Shear stress vs. shear rate for MWNT/PANI nanocomposites based ER fluid.

of an electric field, MWNT/PANI suspension showed a shear-thinning behavior. The plateau region shows Bingham fluid behavior with a yield stress under an applied electric field. The Bingham fluid equation as described below is used as the suitable fluid for the steady shear behavior of many ER fluids [9,10].

$$\tau = \tau_y + \eta\dot{\gamma}, \quad \tau \leq \tau_y$$
$$\dot{\gamma} = 0, \quad \tau < \tau_y$$

τ is the shear stress and τ_y is the yield stress which is a function of an applied electric field. $\dot{\gamma}$ is the shear rate and η is the shear viscosity. MWNT/PANI particles have enhancement of interparticle interactions when applying an electric field. As we increase an electric field strength, the yield stress of MWNT/PANI suspension becomes higher. After the plateau region, shear stress increases with shear rate because the hydrodynamic force dominates the electrostatic force. MWNT/PANI particle chains begin to break down by the shear and the particles do not have sufficient time to realign along the electric field.

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