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Research paper

Synthesized palygorskite/polyaniline nanocomposite particles by oxidative polymerization and their electrorheology

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ABSTRACT

Palygorskite (Pal) clay coated with semiconducting polyaniline (PANI) nanocomposite particles was prepared by oxidative polymerization using aniline monomer in the presence of Pal. The morphological characteristics of the synthesized Pal/PANI composite particles were examined by both field emission scanning electron microscopy and transmission electron microscopy. A rotational rheometer was also used to examine the rheological behavior of the Pal/PANI composite-based electrorheological (ER) fluid when the nanocomposite particles were dispersed in silicone oil. From its flow curve of shear stress vs. shear rate investigated under an applied electric field, the typical ER behavior of the Pal/PANI-based ER fluid was observed. In addition, polarizability and relaxation time of the ER system obtained from the dielectric spectra were well correlated with its ER performance.

1. Introduction

Inorganic–organic nanocomposites have attracted considerable attention for their enhanced mechanical, electrical, optical, and other functional properties (Yilmaz et al., 2007; Kim & Kim, 2008; Meheust et al., 2011; Yin et al., 2011). In particular, clay/polymer nanocomposite particles often exhibit excellent electrical properties when fabricated appropriately (Yilmaz et al., 2007; Meheust et al., 2011). These materials have been adopted as electrorheological (ER) materials (Cheng et al., 2008; Kim & Kim, 2008; Stenicka et al., 2008; Liu & Choi, 2012), in which an insulating medium, such as silicone oil or mineral oil, containing ER particles underwent a structural phase change from a liquid-like to a solid-like form under an applied electric field. A typical type of ER fluid was a colloidal suspension of polarizable solid dielectric or conducting particles dispersed in an insulating fluid, which often exhibits Newtonian fluid behavior in the absence of an applied electric field (Trlica et al., 2000). On the other hand, when an electric field was applied to ER fluids, the dispersed particles became polarized immediately and align along the direction of the electric field, resulting in an increased shear viscosity. Therefore, the rheological behavior of the ER fluid can usually be explained using the Bingham fluid model with the yield stress (Zhao & Yin, 2002; Hiamtup et al., 2006).

Among the various polarizable particles for anhydrous ER materials, semiconducting polymers including polyaniline (PANI) (Adachi et al., 2004; Pavlinek et al., 2005; Hiamtup et al., 2006; Sung et al., 2006), N-substituted copolyaniline (Cho et al., 1998), sulfonated poly(styrene-co-divinylbenzene) (Ikazaki et al., 1998), PANI coated polystyrene particles (Kuramoto et al., 1995), poly(aniline-co-o-ethoxyaniline) (Choi et al., 1999), and poly(acene quinone) radicals (Cho et al., 2005) have been reported. Recently, polymer-inorganic nanocomposites (Yoshimoto, 2005; Maity & Biswas, 2006) and conducting polymer/mesoporous silica hybrids (Cheng et al., 2006) were adopted as dry-based ER materials in addition to various inorganic materials. Among these, the PANI has attracted considerable attention because of its low cost, unique oxidation–reduction chemistry, environmental stability, and excellent optical and electrical properties (Wei & Wan, 2002). The colloidal synthesis of PANI, such as microspheres and nanofibers, can overcome its poor processability. Moreover, assembly structures of these colloids will further improve its properties and expand its applications (Liang et al., 2002; Nandan et al., 2007). PANI and various electro-responsive materials, such as inorganics with high dielectric properties, organic or polymeric semiconducting materials and their composites have been used as ER particles (Yin et al., 2009).

Palygorskite (Pal) is a Mg-rich phyllosilicate with fibrous morphological characteristics, and it can be approximated by the formula, $y Mg_5Si_8O_{20}(OH)_2 \cdot (1 - y)[x Mg_2Fe_2 \cdot (1 - x) Mg_2Al_2]\ Si_8O_{20}(OH)_2$ (Chryssikos et al., 2009). Pal consists of a three-dimensional network of densely packed rods with diameters less than 100 nm and lengths between hundreds of nanometers and several micrometers for each single rod (Pan & Chen, 2007). Pal has a large specific surface area, a moderate cation exchange capacity, and reactive OH-groups groups on its surface that can adsorb and trap metal ions from wastewater (Chen and Wang, 2007). To reduce the cost and improve the comprehensive water-absorbing properties of this material, it is important to fabricate a composite that consists of a polymer and Pal micro-powder (Cui et al., 2012). To enhance the adsorption capacity and selectivity of Pal, considerable attention has been paid to special treatments or modifications

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such as heat treatment, acid treatment (Chen et al., 2007), or graft reactions. (Liu et al., 2007; Chen and Wang, 2009; Shao et al., 2010) Recently, polymers could be grafted successfully onto the surfaces of Pal to achieve the enhanced removal of heavy metals from aqueous solutions (Chen et al., 2009; Liu and Wang, 2007; Wang et al., 2009).

In this study, Pal/PANI composite particles were synthesized by chemical oxidative polymerization. The electrical conductivity of PANI, which is still not high enough for many engineering applications, actually becomes a positive factor for an ER study. An ER fluid was prepared by dispersing the Pal/PANI composite particles in silicone oil, and their ER responses were then investigated using a rotational rheometer under various electric field strengths.

2. Experimental

2.1. Materials

Aniline (5.58 g, 93.13 g/mol, DC chemical, Korea) as a monomer and 200 mL of sulfuric acid (2 mol/l) were used. Palygorskite (7 g, 411.35 g/mol, Fluorochem, UK) was adopted for the nanocomposite preparation. 0.4 M ammonium peroxodisulfate (APS, $(NH_4)_2S_2O_8$, Daejung, Korea) solution was used as an oxidizing agent.

2.2. Preparation of Pal/PANI composite particle

The Pal/PANI composite particles were synthesized by an oxidative polymerization process and used without a post-treatment step except for the doping process. To initiate the polymerization of aniline, sulfuric acid was added drop-wise. At the surface of Pal, the sulfuric acid-modified aniline monomer was polymerized with the aid of APS. The APS solution was slowly added drop-wise into the mixture with vigorous stirring over a period 6 h at room temperature. The obtained Pal/PANI composite particles were centrifuged with deionized water to remove the excess initiator, monomer, and free Pal templates and then dried in a vacuum oven at 60 °C for 24 h.

The electrical conductivity of the Pal/PANI composite particles was about 10^{-3} S/cm measured using a resistivity meter. This value was too high to prepare the Pal/PANI ER fluid. If the sample had too high electrical conductivity, an electric short would damages the rheometer device. The electrical conductivity of the composite particle was then controlled by the de-doping process where the pH was increased to 9.0 by adding a 1 M NaOH solution to an aqueous Pal/PANI solution, and then dried the sample in an oven for 24 h (Strounina et al., 2003; Fang et al., 2007, 2011). The obtained Pal/PANI particles were sieved (mesh size of 38 μm) to remove agglomerated Pal/PANI composite particles for better dispersion of the composite particles as for the ER fluid. As a result, the electrical conductivity of the Pal/PANI composite particles was changed from 10^{-3} S/cm to 10^{-8} S/cm. The 10^{-8} S/cm was in the appropriate range of the electrical conductivity in this ER test.

2.3. Characterization

The particle size and surface morphology were observed by transmission electron microscope (TEM) (CM 200, Philips). To prepare the TEM sample, a grid coated carbon was used. The accelerating voltage of TEM used was 120 kV. The molecular structure of the Pal/PANI composites was detected by Fourier transform infrared (FT-IR, Perkin Elmer System 2000) spectroscopy using KBr pellets in the spectral range from 4000 to 400 cm^{-1}, with a spectral resolution of 4 cm^{-1} and the number of scans of 16. To prepare the FT-IR sample, the sample concentration ratio was 1: 100 (wt%). The elemental analysis of the sample was obtained by scanning electron microscopy (SEM) (S-4300, Hitachi, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) (Horiba, Japan) accessory. The accelerating voltage of EDS used was 15 kV. Both Pal/PANI and Pal were further characterized by a powder X-ray diffraction (XRD, DMAX-2500, Rigaku) ranging from at $2\theta = 5°$ to 90° with Cu Kα (λ = 1.5418 Å) incident radiation at a step size of 0.02°. Scan speed, counting time and slit width of XRD were 0.067°/s, 0.3 s, and 0.8°, respectively. The density of the synthesized composite particles was measured using a gas pycnometer (AccuPyc 1330, Micromeritics Instruments Co., USA). The electrical conductivity was measured by a standard four-pin probe technique using a resistivity meter (Mitsubishi Loresta-GP and Hiresta-UP). An optical microscope (OM, Olympus BX-51, USA) equipped with a DC voltage generator was used to observe the formed chain-like structure of the ER fluid. To characterize the typical ER properties of the ATP/PANI nanocomposite particles (10 vol%) dispersed in silicone oil (ShinEtsu, density = 0.96 g/cm^3) with a kinematic viscosity of 30 cS from the controlled shear rate (CSR) measurements, in which the range of shear rate ranged from 0.01 to 1,000 [1/s] on a log–log scale, the rheological properties were measured using a rotational rheometer (Physica MCR 300, Stuttgart, Germany) equipped with a high voltage generator under different electric strengths. The measurements were at least in duplicate and the experimental error range was within 3%. The dielectric spectra of the ER fluid were also measured using an LCR meter (HP 4284A Precision) with a liquid test fixture (HP 16452A) for liquids to examine their interfacial polarization mechanism. The frequency of the AC electric fields was varied from 20 Hz to 1 MHz.

3. Results and discussion

The morphologies of both Pal/PANI and Pal were examined by TEM to characterize the surface morphology of the pristine Pal (Fig. 1(a)) and Pal/PANI composite particles (Fig. 1(b)).

The surface of Pal was fairly smooth (Fig. 1(a)). Pal has a highly fibrous morphology, forming bundles. The length of each fiber varied from the submicrometer to the micrometer range with an average diameter of approximately 20 nm. In contrast, the Pal/PANI composite particles exhibited a much rougher surface due to the wrapping of PANI (Fig. 1(b)). This means that the polymerization of aniline via a chemical oxidation method onto the Pal template have successfully changed the outside surface.

The chemical interaction between Pal and PANI was confirmed by the FT-IR spectra of Pal/PANI, PANI, and Pal (Fig. 2), which showed marked variations of the absorption bands after modification. Although the Pal/PANI bands had a slight shift owing to the amorphous nature of PANI synthesized by this polymerization, Pal/PANI bands included both their individual characteristic bands of PANI and Pal. In the spectrum of Pal, the bands at 3620 cm^{-1}, 3550 cm^{-1}, and 3420 cm^{-1} were assigned to the stretching vibrations of the Al-OH unit, Mg-OH unit, and stretching vibration of zeolitic water, respectively (Fan et al., 2009; Yin and Zhao, 2011). For Pal/PANI, the wide absorption band at approximately 3446 cm^{-1} was assigned to the stretching vibration of $-NH_2$ and −OH groups (Wang & Wang, 2010), and the Al-OH and Mg-OH vibrations were still visible as minor inflexions in the Pal/PANi spectrum, indicating that PANI had coated Pal. Pal exhibited a band at 1650 cm^{-1}, which was assigned to the bending vibration of zeolitic water and absorbed water molecules (Li et al., 2011). This band was reduced in the Pal/PANI spectrum, suggesting that the zeolitic water and absorbed water in Pal decreased. The characteristic absorption bands of Pal were observed at 1025 cm^{-1} for Si-O-Si, and the band at 980 cm^{-1} corresponding to the stretching vibration of Al–O–Si (Cui et al., 2012). The new bands of Pal/PANI were representative of the C = C stretching vibrations of quinine and benzene rings at 1560 cm^{-1} and 1480 cm^{-1}, respectively. The spectrum of Pal/PANI also showed C-O stretching vibrations at 1300 cm^{-1}, C-N stretching vibrations at 1235 cm^{-1} and C-H out of plane bending vibrations at 800 cm^{-1}, respectively. These results confirm that the Pal surface had been coated successfully with PANI.

The EDS data of Pal/PANI nanocomposite particles are indicated in Fig. 3. This graph shows that the Pal/PANI is composed of C, N, O, Mg, Al, and Si. The synthesized Pal/PANI particle had weight and atomic percentage of C (10.82%, 15.66%), N (9.83%, 12.21%), O (48.60%,