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Synthesis and electrorheological characteristics of polyaniline-titanium dioxide hybrid suspension

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Abstract

Conducting polyaniline (PANI)/titanium dioxide (TiO_2) hybrid particles were synthesized via an oxidation polymerization in the presence of TiO_2, and their electrorheological (ER) characteristics were examined, since the formation of an organic/inorganic hybrid exhibits various advantages from the combination of their unique properties as a part of our efforts to find highly potential ER-active particles using conducting polymers. The TiO_2 nanoparticles possess a relatively high dielectric constant which is important for polarization in the ER response, in which the ER fluids are a class of colloidal suspensions which show a transition from a liquid-like to a solid-like state under an applied electric field. Synthesized PANI/TiO_2 composites in this study were characterized by an FT-IR, thermogravimetry analysis, and scanning electron microscopy. We then prepared the PANI/TiO_2 composites-based ER suspension with insulating oil and investigated its ER behavior as a function of shear rate under an applied electric field. The fast relaxation time of PANI/TiO_2 hybrid was expected to enhance electrostatic force over shear force under a shear flow, showing the improved ER performance. Furthermore, it was also found that the properties of TiO_2 affect the dielectric of PANI/TiO_2 composites to give better ER properties.

Keywords: Electrorheology; Polyaniline: Titanium dioxide: Hybrid: Suspension

1. Introduction

Recently, organic-inorganic composites have played an important role in improvement of their material characteristics [1], such as mechanical, chemical and optical properties. They include polyaniline (PANI)/$BaTiO_3$ composites [2], PANI/V_2O_5 composites [3] and polymer/clay nanocomposites with either PANI or polypyrrole [4]. However, to incorporate the inorganic component into the conducting polymers effectively, appropriate synthesis techniques have to be followed [5, 6]. As one of these techniques, inorganic nanoparticles can be introduced into the matrix of a host-conducting polymer by a chemical method [7].

The conducting PANI/ titanium dioxide (TiO_2) composites which exhibit high piezosensitivity at a certain PANI/TiO_2 composition have been investigated [8]. Because of the combination of electrical conductivity of PANI and UV-sensitivity of anatase TiO_2, such nanomaterials are expected to be applied in electrochromic devices, nonlinear optical system, and photo electrochemical devices.

PANI has been considered as one of the most potential conducting polymers due to its high conductivity, resulting from its easy preparation and thermal stability. Therefore, it has been applied to various electronic devices such as chemical sensors, electrochromic display, smart window, and light emitting diode [9] via easy control of conductivity [10].

On the other hand, titanium with a good ductility, light weight and corrosion resistance has been applied to various engineering fields such as capacitor, aircraft, vessel component and paint despite of its low thermal and electric conductivity [11, 12]. Especially, due to highly dielectric constant, it has been widely used as a ceramic capacitor.

Electrorheological (ER) fluids are suspensions of dielectric or semiconducting particles in a nonconducting liquid, and exhibit a remarkable change in rheological properties, including a drastic increase in apparent viscosity, as well as the formation of reversible microstructures under an applied electric field [13]. Due to their fast response time and controllable or tunable shear viscosity, ER fluids have been widely used as smart and intelligent materials for various engineering applications, including shock absorber, actuator, brake, and seismic controlling frame structures.

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Table 1.
Electrical conductivity of $PANI/TiO_2$ composite and dedoped $PANI/TiO_2$ composite

Sample	Conductivity (S/cm)
$PANI/TiO_2$ composite	2.41×10^{-3}
Dedoped $PANI/TiO_2$ composite	3.79×10^{-9}

As ER materials for anhydrous systems, various semiconducting polymers such as PANI and its derivatives, polypyrrole, polyphenylenediamine, and inorganic materials including polymer/clay nanocomposites with PANI and polypyrrole have been used for particulates in ER fluids [14-17]. In this study, as a new ER material based on the PANI, conducting $PANI/TiO_2$ hybrid particles [8] were synthesized by an oxidative polymerization [18], and characterized via an FT-IR, TGA, SEM and rheometer. We put our effort on combining material properties of an electrical conductivity and a highly dielectric constant for an electrorheological (ER) material. $PANI/TiO_2$ particles exhibit a higher polarization phenomenon than that of PANI particles. Apparently, the $PANI/TiO_2$ particles are found to have a good ER performance, due to its high polarization [19].

2. Experimental

Initially, PANI was synthesized via an oxidative polymerization from aniline monomer 20g (Junsei Chemical, Japan, 99%) with 1M HCl (Ducksan Chemical, Korea, 35%) aqueous solution. The molar ratio of 1.2 of an ammonium peroxy disulfate (APS)/aniline was employed, in which the APS (61.88g) (Daejung, Korea, 98% of purity) was used as an initiator.

Concurrently, the $PANI/TiO_2$ particles were synthesized by an in-situ polymerization in the presence of hydrophilic TiO_2 nanoparticles (R900, Dupont, USA) in which the TiO_2/aniline weight ratio of 0.25 was applied. The pH of $PANI/TiO_2$ composites was adjusted through a dedoping process with 0.1M NaOH (Daejung, Korea, 98% of purity). We modified the surface of TiO_2 dispersed in 1M HCl solution. After that, the surface characteristics of TiO_2 showed its change of electrical property from negative to positive charges which was confirmed by a zeta-potentiometer. In this way, pre-treated TiO_2 was added to the reactor with 1M HCl by stirring (200 rpm) at 0℃. Aniline was added to the reactor by stirring for 3 h at 0℃. The APS as an initiator dissolved in 1M HCl was dropped into the reactor for 2 h. After dropping the initiator, the reaction was maintained for 24 h. $PANI/TiO_2$ composites were filtered and washed with distilled water and methanol until the filtrate becomes colorless, and then dried in oven for 24 h [20].

Electrical conductivity of the pellets at room temperature was measured by a standard 2-probe method using a picoammeter (Keithley 487, USA). Since the pristine $PANI/TiO_2$ composites right after the synthesis were unsuitable for the ER test because of its high conductivity, we controlled their conductivity via a dedoping process of the particles using NaOH [21], while checking the change of pH at every 3 hour during this dedoping process. Using both HCl and NaOH, we maintained pH to be 9 by a titration. We prepared 10 vol% ER fluid of which the $PANI/TiO_2$ composites were dispersed in silicone oil (dynamic viscosity: 50cS, density: $0.96 g/cm^3$), using sonicator about 1 hour in order to obtain good dispersion.

Characterization of the composites was performed using SEM (Scanning electron microscope, S-4300, Hitachi), TGA (Thermogravimetric analysis, Q50, TA instrument) and FT-IR (Perkin Elmer). ER property was characterized by a rotational rheometer (MCR 300, Physica, Germany).

3. Results and discussion

Electrical conductivities of both $PANI/TiO_2$ composites and dedoped $PANI/TiO_2$ composites are described in Table 1. Compared to the conductivity of $PANI/TiO_2$ composites of 2.41×10^{-3} S/cm, the conductivity of the dedoped $PANI/TiO_2$ particles was decreased to be 3.79×10^{-9} S/cm.

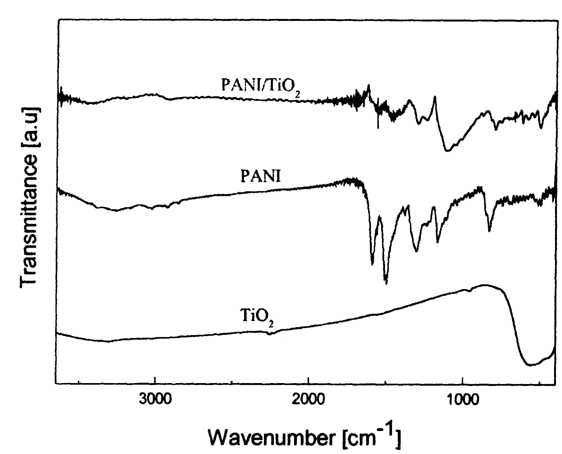

Fig. 1. FT-IR curve of PANI, TiO_2 and $PANI/TiO_2$ composites

In addition, from the FT-IR spectra of the TiO_2, PANI and $PANI/TiO_2$ composites, we can find their very