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Conducting polyaniline-wrapped sepiolite composite and its stimuli-response under applied electric fields

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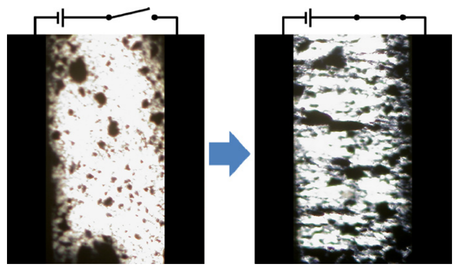
HIGHLIGHTS

- Fibrillar-shaped sepiolite was adopted to fabricate its nanocomposite with polyaniline.
- Nanocomposite shows a typical electrorheological (ER) behavior under electric field.
- ER characteristics were well correlated to their dielectric spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

Conducting polyaniline (PANI)-wrapped sepiolite (SPL) composites were prepared using an in situ oxidative polymerization process and evaluated as a potential electrorheological (ER) material. The morphology of both SPL and the PANI/SPL composite were confirmed by scanning electron microscopy and transmission electron microscopy. The synthesized PANI/SPL composite was also analyzed by physisorption analysis, Fourier transform infrared spectroscopy and thermogravimetric analysis. Their ER properties when dispersed in silicone oil were investigated using a rotational rheometer under different applied electric field strengths, and their shear stresses could be fitted well using the Cho–Choi–Jhon model equation.

1. Introduction

Electrorheological (ER) fluids, which solidify under applied electric fields in the order of kV/mm, are suspensions of polarizable particles dispersed in a non-conducting liquid [1–5]. Under an applied electric field, these polarized particles behave as electric dipoles that link with each other to form chains, exhibiting a rapid (in the order of milliseconds) phase transition from a fluid-like state to a solid like state in the direction of the applied electric field [6–8]. The dramatic increase in shear viscosity with a rapid response time originates from the substantial alteration of the suspension structure, particularly the field-induced formation of fibrous aggregates aligned with the electric field [9]. All the physical and mechanical properties of the suspensions induced by the applied electric field are reversible [10].

Recently, a range of anhydrous ER fluids containing semiconducting polymers, such as polyaniline (PANI) [11] and its derivatives, poly(acenequinone) radicals [12], polyphenylenediamine [13], and polypyrrole [14] along with inorganic materials [15,16] were investigated. These ER materials have advantages over a wide working temperature range, and reduced device abrasions operating at a relatively low current density, possessing intrinsic charge carriers in either bulk particles or their surfaces that can move locally under an applied electric field [17]. PANI is a favorable conducting polymer that has been adopted in this ER field

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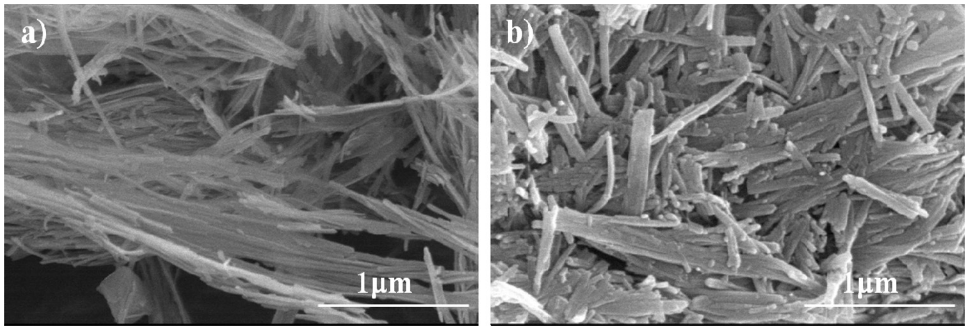

Fig. 1. SEM image of (a) SPL and (b) PANI/SPL composite.

because of its easy synthesis, thermal and chemical stability, high sensitivity to an electric field and controlled conductivity using a doping/dedoping process [18–20].

Clays have attracted significant interest both in academia and industry because of their large specific surface area, high aspect ratio, excellent mechanical performance, outstanding chemical, thermal and dimensional stability, low cost, and other unique properties [21]. Sepiolite (SPL) is a type of natural fibrillar silicate clay, and its fibrillar single crystal is the smallest structure unit with a length of 500–2000 nm and a diameter of 10–25 nm [22]. SPL with a chemical formula of $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4{\cdot}8H_2O$ is a hydrous magnesium silicate as the unit cell structure with a high specific surface area [23]. The complex ribbon-layered SPL structure is composed of blocks, forming a capillary network of parallel channels. The blocks are characterized by a sandwich structure of two layers of tetrahedral silica on the outside and a central layer of octahedral sheets of magnesium oxide hydroxide [24,25]. Owing to the discontinuity of the silica sheets, silanol groups are present on the external surface of the silicate particles [26]. The large specific surface area and high porosity of SPL account for its remarkable adsorptive properties that make it a promising material for a wide range of applications [27] including ER fluid [28]. In particular, in the area of filler materials, SPL has already shown not only mechanical reinforcing capability in polymeric matrices, [29–31] but also improved rheological properties and thermal stability [32,33]. It can be also noted that various PANI hybrids with different types of inorganic particles such as bentonite [34,35], kaolinite [36] and titania [37] have been also applied for ER fluids, exhibiting different characteristics depending on the morphology of PANI.

In this study, a PANI/SPL composite was synthesized via in situ polymerization using ammonium persulfate as an initiator. This composite was dispersed in silicone oil for ER fluid characterization, especially regarding a flow curve behavior and yield stress from a steady state test and stress relaxation from a dynamic oscillation test compared to previously reported work [28]. Their ER properties were found to exhibit improved flow behavior and yield properties.

2. Experimental

2.1. Synthesis of PANI/SPL composite

Aniline (DC Chemical Co., Korea, 0.3 g) and hydrochloric acid (HCl 35%, DC chemical Co., Korea. 6 ml) were added to 200 ml distilled water, and SPL (Sigma–Aldrich, 3 g) was then dispersed into the mixture in three-neck round bottom reactor with vigorous stirring for 2 h. For the polymerization of aniline, 10 ml of an acidic aqueous solution (containing according ammonium persulfate (Daejung Co., Korea, 1.36 g) and concentrated HCl (1 ml) was added dropwise to the mixtures within 0 °C for 12 h with continuous stirring. After polymerization, the reactant mixture was centrifuged, and a black powder composite was obtained. The product was washed several times with water until it became neutral and dried under vacuum oven at 60 °C overnight.

The synthesized PANI/SPL composite was dedoped by controlling its pH to 9.0 using an aqueous NaOH (1 M) solution and being kept for 1 day to control its electrical conductivity to a proper range for its ER application.

For the ER fluid, the resulting PANI/SPL composite particles (8 vol.% particle concentration) in silicone oil (KF-96-50cS grade, Shinetsu, Japan) were prepared by sonication.

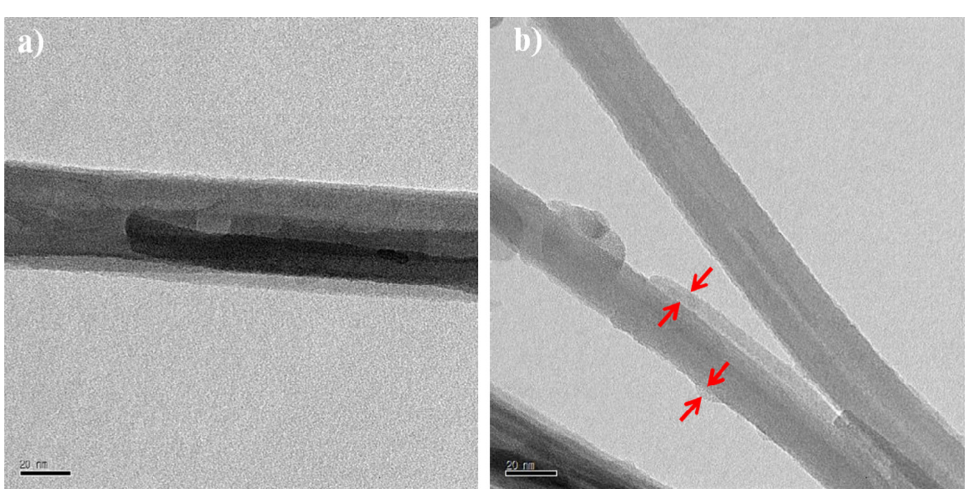

Fig. 2. TEM image of (a) SPL and (b) PANI/SPL composite.